











"THE ENGINEER" SERIES.

# WHAT INDUSTRY OWES TO CHEMICAL SCIENCE.

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## INTRODUCTION.

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**AMIDST** the flood of opinions and advice on the relations of science to education and industrial prosperity with which we have been deluged during the past two or three years, we may turn with welcome relief to the unembellished records of work done and of ends accomplished which the authors have here presented for our enlightenment and encouragement. The majority among us stood much in need of enlightenment on this subject, and many of us will feel grateful for the encouragement which is to be derived from these records of past achievement. These records supply a complete answer to a question with which most chemists have had to deal at one time or another during their career : what is the place of the chemist in practical life, and what part has he taken in industrial and social development ?

The engineer ministers to the comfort and convenience of the community in ways which can hardly escape the notice even of the man in the street. The Forth Bridge, the ocean greyhound, the motor car and the aeroplane are at once recognised as the fruits of his skill and energy,

but for the most part, the work of the chemist is inobvious, and is little, if at all, understood. But the chemist and his half-brother, the metallurgist, have all the time been hard at work in the background, helping to provide the engineer with metals and other materials of new and improved qualities, without which he could not have produced the machines and structures which represent the triumphs of his art.

In many other directions chemistry has been the handmaid of arts and crafts, which make their appeal to the public on far other grounds than those of the chemical and other scientific help they have laid under contribution.

But chemistry also has its own triumphs, and those who will take the trouble to study this work will be rewarded with visions of achievement in this field which they had not hitherto dreamt of.

These records ought to prove stimulating and suggestive to those whose sons and daughters have not yet selected a calling or profession. The place of chemistry in the national life has been far more important than the majority of educated people have imagined, and this place bids fair to become of vastly increased importance in the near future. The special message for parents and teachers is, therefore, that trained chemists will, in the near future, be in increased demand for industrial and official positions.

For the responsible teachers of chemistry there are other messages also, if they care to seek for them; for from these records of achievement much may be learned as to the actual needs of industry on its scientific side, and as to the types of workers who will have to be trained if these needs are to be properly met.

The great body of teachers of science on the one hand, and the still greater body of manufacturers on the other hand, have been equally at sea as to how (a) the results of scientific discovery, and (b) the young graduates in science who are prepared at our universities and colleges, can best be utilised in industry. Speaking broadly, the teachers of science do not know the needs of industry, either in regard to the nature of the problems which await solution, or to the kinds of trained experts who will be required to take part in the more highly organised industries of the future. Again, speaking broadly, manufacturers and leaders of industry are equally at a loss as to the means whereby scientific discovery, scientific methods and scientifically trained men can be used most effectively in the development of the industries for which they are responsible.

Fortunately, there are already lines of communication open between these two important bodies, and the hope for the future is that these lines may be broadened out into a common ground on which

mutual understanding will be reached and where practical schemes of development will be developed.

Much can, undoubtedly, be done to improve the training of chemists for practical life. It is in the laboratory that the foundations of this training must be well and truly laid by sound training and ample practice in manipulation and methods. Not only manipulative skill, but resourcefulness and the power of organising routine work ought to be acquired in the laboratory, if the training is on the right lines. On the foundations thus laid, a super-structure of knowledge of physical, mechanical, and chemical laws can be securely built. But a scientific equipment, however sound, is not in itself sufficient; it is of equal importance that the young chemist throughout his training should be thoroughly imbued with the spirit and aims of the successful leaders of industry. Nothing will so surely awaken in the student an appreciation of practical aims as a wisely directed study of the achievements of science in industry. The present work will supply teachers of chemistry with abundant material for the purposes of this study. This study ought not, however, to displace the parallel study of the steps by which chemical theory has been evolved by the deep insight and the patient observation and experiment of the great leaders in chemical science. It ought to be made clear to the student that, though in one sense

the two aims, the attainment of knowledge for its own sake, and its attainment as a means to practical ends, are at opposite poles, yet that there is no real antagonism between them, each is complementary to the other. There are intellectual triumphs to be won in the application of science as well as in its pursuit for its own sake.

The deeper and more prolonged search into the phenomena and laws of Nature must, of necessity, be left to those who by natural endowment and by opportunity can pursue this search apart from the distractions of the work-a-day world. The workers on the applications of science may well realise their debt to these seekers after knowledge, for the seeds of achievement on the practical side must, in many cases, be planted and watered under their fostering care.

During the past three years the scientific developments of modern warfare have been the means of bringing the workers in pure and in applied science into touch to an extent which would have appeared almost impossible in pre-war times. There are encouraging evidences that this new co-operation has been appreciated on both sides, and that a return to the former condition of isolation would be regarded as most unfortunate.

The authors have wisely disclaimed any attempt in this work to present the extraordinary wealth of material at their disposal in anything like its true

proportions and perspective. The precious stones in the necklace have been strung together rather with an eye to their collective preservation than to their artistic effect as a whole. Apart from the reasons for this, which the authors themselves have given, I am inclined to think that for the serious purpose they had in view, the method has much to commend it. The central object was not to present a pleasing and finished literary work which would gently stimulate the imagination of the general reader, but to set forth in their bare simplicity the broad facts of achievement, leaving each case to make its own appeal.

In conclusion, I would express the hope that this work will not only be widely read by the general public, but that it will be cordially welcomed by those who are most deeply concerned in the future of British industry.

GEORGE BEILBY.

## PREFACE.

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IN recent times, and especially during the war, a great deal has been written and said on the benefits derived from the applications of science to industry ; the subject has been discussed in the technical and daily Press, and in monographs devoted to particular industries ; but, for the most part, it has been dealt with in the abstract or with very limited reference to the actual results achieved.

The contents of this volume appeared as a series of articles published in *The Engineer* during the seven months December, 1916, to July, 1917, inclusive, under the title of "What Industry Owes to Science." The articles were not intended to embrace subjects of common knowledge to the engineer, in which the influence of physical and mechanical science would have claimed greater attention, but dealt mainly with chemical science. For that reason the title of the work has been modified ; the text, however, remains practically the same.

The object was to take each industry in turn, and to show by examples how science had advanced the methods and processes of production



and had laid the foundation for the establishment of new manufactures.

The work covers a survey of many important industries, presented in such a manner that the substance is not altogether out of the depth nor beyond the interest of the educated public. We hope that it may be especially useful to students of chemistry and engineering, as affording them an indication of the vast field open to them in their professional careers, work in which it may be anticipated that there will be increasing activity and boundless scope in the near future ; and that it will find a place in the offices of men of business in many branches of commerce, and of public companies concerned with productive industries, as well as in the libraries of Chambers of Commerce and Trade Associations.

A bibliography is provided, including many useful books referred to during the preparation of the work.

The authors desire to express their deep indebtedness to Sir George Beilby for his kindness in contributing an introduction, which they feel has very greatly enhanced the value of the volume.

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London, 1917.

## WHAT INDUSTRY OWES TO CHEMICAL SCIENCE.

### CHAPTER I.

#### MINERALS AND METALS.

WE have heard a good deal lately of our neglect of science, particularly of applied science—and we are prepared to admit that this country has been behind other countries in realising the importance of scientific principles in industry. The fact remains, however, that though we have been so remiss, we cannot have ignored science entirely, or surely the position of our industries—those that are left to us—to-day would not be what it is. Instead of pursuing the subject in the abstract, we propose in a few brief chapters to deal with accomplished facts; to show by illustrative examples the extraordinary developments directly attributable to scientific thought and method and the benefits derived therefrom by the community. The whole art of engineering is based on physical and mechanical science, and the materials employed in this art are dependent in some degree on the science of chemistry. This country has never lacked engineers of the first order, and, therefore, if we may judge by their works, we must conclude that their science has been as truly founded as their structures, and their materials must likewise have been suitable for their purpose. Clearly, then, we have not been lacking, the aid of physicists, mathematicians, and chemists in the art of engineering and all that the term denotes. The materials of construction cannot be used intelligently unless the engineer has a proper

knowledge of their physical powers of withstanding stress and strain, as well as of their chemical properties, including their internal structure and power of resistance to air, fire, water, and other agencies.

The subject is so vast and its ramifications so diverse that it is difficult to deal with it without being drawn into the production of a text-book, but we will endeavour to keep to the principal aim of showing the influence of science in industrial progress.

Our methods of utilising science may be wrong, and there may be room for great improvement, but the impression is gaining ground that in the habit of decrying ourselves and our doings we have overshot the mark. We have used science more than we realise, but have not talked about it as much as some other people. We know, for instance, several Sheffield steel firms who employ thirty to forty chemists and are in constant touch with the most experienced men of science interested in this branch of industry. We know also that both in the directorate and in the control of the actual processes of manufacture in the works the industry is coming more and more under the personal supervision of scientific men, that new laboratories are being equipped, and that science in the steel industry is now very much to the fore.

#### STEEL.

German delegates to the meeting of the Iron and Steel Institute held at Sheffield in 1905, freely admitted that Germany had much to learn from that centre and no doubt derived benefit from the hospitality then extended to them. The reputation of Sheffield in steel production dates from 1740, when Huntsman discovered the process of casting completely fused metal from crucibles. Sixty years ago steel was obtained by decarburising pig iron to malleable iron in a puddling furnace and subsequently introducing the requisite amount of carbon by the cementation process. These operations were protracted, required exhausting labour, and involved the use of large and expensive furnaces

subjected to considerable wear and tear and consuming large quantities of fuel.

In 1856, Bessemer—a scientific man—as the result of experiments deliberately directed to a definite object, introduced his process for “The Preparation of Steel without Fuel.” He found that by forcing a blast of atmospheric air through molten cast iron, contained in a suitable vessel lined with ganister, a siliceous material, the oxidisable impurities in the iron could be removed without the external application of heat, since the heat produced by oxidation was sufficient to keep the mass in a molten state. Manual or mechanical stirring was unnecessary. The pig was melted in a cupola, and transferred to a mixer of up to 600 tons capacity. From the mixer a charge was conveyed by a ladle to the converter, the latter being swung into position after the “blow” had been started. In twenty minutes the operation was completed; the blast was stopped for a few seconds while a workman threw in from a shovel sufficient spiegel or ferro-manganese to introduce the proper proportions of carbon; the blast was started again for a short time to mix the metal and the charge was immediately poured into moulds.

Contrast the rapidity and simplicity of this method with the time and labour expended in the other. Cementation alone required seven to ten days; the equivalent effect, after Bessemerisation, occupies only the time required to add the spiegel and re-mix the charge. The fuel expended is only that used in the cupolas, and even that is obviated in some cases where the constancy of grade of pig from the blast-furnaces can be relied on, when the pig is taken direct from the blast-furnace to the converter.

The original or acid Bessemer process had, however, two disadvantages:—(1) phosphorus and sulphur could not be removed owing to the reduction of their oxides by iron and, therefore, only special “Bessemer pigs,” free from phosphorus and very low in sulphur, could be used; (2) the ingots produced contained blow-holes. Science overcame the first of these disadvantages. In 1879 Thomas and Gilchrist found

that by lining a converter with burnt dolomite or magnesite, instead of ganister, and by adding a quantity of lime to the charge, the whole of the phosphorus and some of the sulphur could be removed.

This was the result not only of scientific methods of research but of the direct application of a scientific principle, viz., that of using a basic lining and adding lime, a basic material, to retain the acidic substances produced by the oxidation of phosphorus and sulphur. The second problem, however, was solved by the empirical discovery that the addition of a very small quantity—5 to 8 oz. per ton—of aluminium to the molten metal minimised the formation of blow-holes.

The only important rival to the Bessemer method is the open-hearth process, perfected about twelve years later by Sir William Siemens and his brother—both scientific men. After great initial difficulties, they succeeded in decarburising iron without contact with solid fuel. In this process an exceedingly high temperature is produced in an oxidising atmosphere by the combustion of a mixture of producer gas and air fed into the furnace. Changes take place of the same character as in the Bessemer process. Both acid and basic hearths are used, and the principle of regenerative heating is utilised.

To Dr. Sorby, of Sheffield, we owe the introduction of metallography, and in this connection the names of Osmond, Martens, Stead, Roberts-Austen, Sauveur, and Le Chatelier, all men of science, must be remembered. Up to the present day, and for some years past, the microscopic examination of the etched surfaces of metal has been common practice in steel works laboratories. Researches on the cause of recalcence, combined with the intimate knowledge of the structure of steels afforded by microscopic examination, have placed in the clear light the equilibrium relations of iron and carbon, and have thus changed rule-of-thumb experience into sound scientific principle. Our views on the physical and chemical nature of these equilibrium relations have been changed by the progress of research. Explanation by means of the solution theory has replaced that based on the theory of the allotropy

of iron, and our knowledge of the subject is thus becoming more definitely established. To be able to explain a phenomenon is second only to knowing that the phenomenon will occur. Whereas rule-of-thumb or empirical discoveries may occasionally give us good results, science, organised knowledge, enables us to proceed on definite lines.

The discovery of rarer metals has led to the manufacture of many varieties of steel, including alloys of special hardness. The properties of special steels and their behaviour under varying conditions, the bearing of the character of their internal structure and similar questions have formed the basis of numerous researches which have rendered the industry in an increasing degree more exact and scientific. The researches of Sir Robert Hadfield have resulted in supplying us with special steels differing from ordinary steels, through the addition of various elements other than those commonly present, whereby they acquire properties of enhanced hardness, toughness, elasticity, &c.

Thus, by adding 7 to 20 per cent. of manganese we ensure great strength and toughness, the well-known Hadfield steel ordinarily containing about 13 per cent. of manganese and 1 per cent. of carbon; the addition of about 3 per cent. of nickel and 0.2 per cent. carbon gives us a steel of tensile strength and elasticity suitable for the manufacture of gun barrels; and the addition of 2 to 3 per cent. of chromium with about 1 per cent. of combined carbon gives a remarkable steel which, when hardened and tempered, is employed in the manufacture of locomotive tires and springs, armour plates, armour-piercing projectiles, and certain qualities of files. Similarly, the introduction of titanium, molybdenum, tungsten, aluminium, vanadium, and boron gives varying effects now easily obtainable by the scientific steel maker.

These examples serve to illustrate clearly the advantages gained by the application of scientific knowledge in the production of one of our chief materials; but the function of the chemists in a steel works or any works is not confined to devising pro-

cesses or producing varieties of the products. They are concerned with problems of many kinds, and among these the question of fuel and fuel economy both in raising power and in smelting operations are of primary importance. Science determines the suitability and value of the coal employed. Tests are made to determine the calorific power and to estimate the sulphur, ash, and the volatile matter, including moisture, all important factors from the point of view of economy. The manufacturer who ignores these questions must suffer through the employment of coal containing sulphur which attacks his fire-boxes, and the purchase of water and useless mineral matter. Next, the treatment of boiler-feed water where the supply is not naturally soft must not be neglected, or the accumulation of scale will result in waste of heat, inefficient working, and other deplorable conditions. The method of water softening, by the addition of lime, was established by Dr. Thomas Clark, Professor of Chemistry at Aberdeen University, from 1833-39, and its importance in every industry involving the use of boilers, or requiring the use of soft water, must have been and still is inestimable.

#### NON-FERROUS METALS.

Mining and metallurgical industries are essentially scientific, calling for the services of chemists (1) on the mines, to examine ores, to advise on their concentration and generally to specify the methods to be adopted for the extraction of metals, and (2) in the actual working of the metal.

The production of non-ferrous metals, such as copper, lead, zinc and aluminium, needs the help of trained technologists whose labours are constantly directed to the discovery of improved processes and of new varieties of alloys adapted to special purposes, particularly those demanded by the trend of engineering development.

In surveying the history of non-ferrous metallurgy, the most striking feature is the extent of comparatively recent scientific advancement. In many cases the methods of treating ores to obtain crude metal

remain fundamentally the same as when they were originally discovered—for the most part empirically ; but they have been explained, modified, and improved by science ; while in other cases, new and better methods, due solely to science, have been substituted for old ones.

*The Separation of Minerals.*—The ores of heavy metals are frequently of such low grade that the metal cannot be won economically. Thousands of tons of valuable minerals would still remain unworked except for the scientific methods of concentration now employed. An ore containing only one per cent. of tin will repay treatment. It cannot be smelted, but a complex process of table washing, roasting, and washing again concentrates it to 60 to 70 per cent. ready for the smelter. Low grade sulphide ores and graphite ores are concentrated by one or other of various methods of oil separation and flotation which afford interesting examples of discovery originated in empiricism, developed by chance discovery and mechanical ingenuity and further improved by the direct application of scientific thought, whereby their utility has become widely extended so as to effect invaluable economics in the mineral industries. Although various theories have been advanced to explain the phenomena of flotation, the true mechanism remains as yet obscure. It is instructive to follow the stages of the advances made in this direction, and to indicate the present views on the subject.

In 1886 Carrie J. Eversen found that sulphide mineral particles could be separated from the gangue in ores by kneading the finely crushed ore with a paste formed by the action of sulphuric acid on certain oils, *e.g.*, linseed or cotton seed. The oil adhered to the particles of sulphide mineral and bound the whole into a coherent mass. The gangue was then washed away by water. The process was very little used, its application being limited to rich pyritic gold ores, the treatment of which was profitable.

The next development, patented by Elmore in 1898, was an oil separation process wherein the finely



crushed sulphide ore made into a pulp with water was well mixed with 3 to 6 per cent. of its weight of residuum oil. The oil floated to the top and formed a layer carrying the sulphides, leaving behind the gangue. The top layer was separated by means of a spitzkasten and the oil run into a centrifugal machine containing warm water, where some of the oil was separated to be used over again. The partially de-oiled concentrates were further treated in a smaller centrifugal to effect a further separation of oil, and were then ready for the smelter. In 1901 Elmore patented the use of sulphuric acid in the process, as an aid to the production of cleaner concentrates. The process was not generally adopted because the losses of oil due to entanglement in the gangue pulp were very high.

The Elmore vacuum method was an outcome of the above. This is an oil flotation process, as distinct from an oil separation process. The pulp of ore and water, mixed with a very small quantity of oil and enough sulphuric acid to make the mixture slightly acid, is exposed to a partial vacuum; the air dissolved in the water rises up through it in the form of bubbles, floating the oiled sulphides to the top, whence they are drawn off. From a 2 to 3 per cent. copper ore, concentrates of up to 20 per cent. can be produced.

In 1901 C. V. Potter, working on Broken Hill ore, heated the crushed ore in an acid water pulp. The action of the acid upon carbonates in the ore generated carbonic acid gas, which, rising to the top, carried sulphide mineral with it. In 1902, in connection with this process, G. D. Delprat used salt cake instead of sulphuric acid.

In 1903 Cattermole, by adding 4 to 6 per cent. of oleic acid to the ore-water pulp and applying slow agitation, caused the sulphide particles to aggregate into large granules with the oil. The gangue which remained in the pulp was then separated by means of an up-cast. The principle of the method was good, but the expense in oil was large. It was in connection with the work on this process, however, that the froth

flotation process was discovered. By using small quantities of oil—up to 0.1 per cent. calculated on the ore, though less generally—and churning up the pulp with air by rapid agitation with a special paddle, the oiled sulphide particles are caused to rise to the top as a strong froth which is floated off by a spitzkasten. This process especially has been developed by scientific research, and the efficiency and the economy of ore concentration have been thereby greatly improved. Sulphide ores of zinc, copper, lead, iron, antimony, molybdenum, and of other metals are very efficiently treated. Tin-stone-pyrites table concentrates are separated, the pyrites being floated off; and graphite is easily concentrated to an exceedingly clean product. The grade of the concentrates is high and the recovery excellent. The use of acid is sometimes necessary to produce clean concentrates, enough being added to ensure an acid reaction in the pulp. Curves can be plotted showing the variations in grade of concentrates and recovery with variation in the amounts of oil and acid used. The testing of ores is scientifically carried out in special apparatus. The experimenter not only finds the best method for treating the ore, but also observes and records any peculiarities exhibited that may be of use in furthering the aims of the process or may serve to throw light on the ultimate causes of the principles underlying the method. Wood's modification of the above process renders it possible to concentrate certain ores without the use of oil.

These concentration processes are of comparatively recent invention, and are increasingly applied to the treatment of low grade sulphide ores and the tailings from table concentrations.

Experiments on the flotation of other minerals, such as native copper, gold, and Scheelite, an ore of tungsten, have met with success, and will probably be greatly developed during the next few years. The flotation of carbonate and other oxidised ores has been attempted with positive results, but this extension also is as yet in the experimental stage. The general opinion of men of science at the present day

is that flotation is an effect of surface tension, though some favour the view that the mineral particles must also carry an electric charge. The ultimate causes can only be established by further research.

In dealing with the separation of minerals we should mention also the important work of electrical and mechanical engineers, to whom much credit is due for the invention of magnetic separators. Many ores containing magnetic minerals are now efficiently treated by these machines, involving both wet and dry methods. As instances may be taken the magnetic concentration of magnetite ores, and the separation of this mineral from pyrites. Magnetic separation has also been applied in the treatment of monazite sands for the concentration of thorium, to which we will refer later.

*Copper.*—Scientific knowledge has come to the aid of the copper smelter and refiner in various ways. The introduction of water-jacketed blast furnaces—such as are used in lead smelting—in the fusion for regulus, has reduced wear and tear to the minimum. These furnaces are made of iron and are double walled, with water circulating through the space between the walls, producing a cooling effect inside the furnace in the immediate vicinity of the wall. The result is that some of the molten slag solidifies on the wall, forming a protective coating which is not further attacked, since the liquid does not corrode it, and thus the iron walls of the furnace scarcely come into contact with the liquid.

A method of smelting pyritic copper, silver, or gold ores by the heat of oxidation of the pyrites, without the aid of any other fuel was introduced as recently as 1905; in actual practice, however, up to 5 per cent. of carbonaceous fuel is now added. Water-jacketed blast furnaces are used, and air—pre-heated in some cases—is liberally supplied through a large number of tuyeres.

Copper intended for use as an electrical conductor must be of high quality, the presence of very small quantities of certain other bodies causing a marked diminution in its efficiency. The necessary degree of

purity can now easily be obtained by the methods of electrolytic refining. A thin sheet of electrolytic copper forms the cathode, a slab of blister copper the anode, and the electrolyte is an acidified solution of copper sulphate.

Pure copper is deposited on the cathode, the anode being gradually dissolved. Impurities in the copper, such as iron, zinc, nickel, &c., of which the sulphates are soluble, are allowed to accumulate in the solution until their quantity renders the liquor inconvenient to deal with. At this stage the copper in the liquor is precipitated with metallic iron and fresh solution substituted. Other metals present, such as platinum, gold, silver, lead, and arsenic, form a fine mud in the bath, and this mud is afterwards treated for recovery of the precious metals. Thus, by this scientific method, not only is copper obtained in a very pure state, but the gold, silver, and platinum also can be extracted profitably.

*Lead.*—A remarkable instance of the application of pure science to the solution of a technical problem is provided in the methods employed in the desilverisation of lead by the Pattinson and the Parkes methods. Before 1833 the only available process was cupellation, and this could only be effected economically if the lead contained 8 oz. per ton or more of silver. Therefore much silver remained in the lead, of which, in the aggregate, large quantities contained less than this amount. The method patented by Hugh Lee Pattinson in 1833 depended on the fact that when a solution is partially frozen some of the solvent separates in the solid form, leaving a solution richer in the dissolved substance. For instance, when salt water is frozen, pure ice separates and the remaining solution is stronger in salt. Molten lead containing silver may be regarded as a solution of silver in lead, and if this solution is allowed to solidify partially, almost pure lead separates out in crystals. Two methods are adopted, that of thirds and that of eighths. Usually, sixteen kettles, lined with lime to prevent attack by litharge and holding about 12 tons each, are employed. For lead comparatively rich in

silver, two-thirds of the contents of each pot are removed as lead crystals; and for lead which is poorer in silver, seven-eighths of the contents is removed from each pot. In the latter case fewer pots are required. By these means, respectively, starting from a lead containing up to 3 oz. of silver per ton, a silvery lead containing 700 oz. per ton, and a "pure" lead containing only  $\frac{1}{4}$  oz. to  $\frac{1}{8}$  oz. of silver per ton can be obtained. The process in each case is stopped when the silver reaches about 700 oz. per ton, as this is approaching the eutectic.\* A modification of the method has been introduced whereby the lead is cooled more quickly by blowing in steam and spraying the top of the lead with cold water, the rich silvery lead being poured off from the crystals instead of the latter being baled out.

The silvery lead obtained by either process is cupelled on a hearth made partially of bone ash, which absorbs most of the lead oxide. Some of the litharge produced is blown over the side of the cupel by the blast of air, and is used in the manufacture of paint.

The Parkes process depends upon the fact that silver is much more soluble in zinc than it is in lead, whilst lead and zinc are mutually soluble only to a small extent. A saturated solution of zinc in lead contains only about 1 per cent. of zinc whilst a saturated solution of lead in zinc contains 2 to 3 per cent. of lead. If, therefore, molten argentiferous lead is stirred up with molten zinc the latter extracts most of the silver from the lead and when the stirring is discontinued rises to the top, forming a separate layer. An exactly parallel operation frequently used in the laboratory is the method of extraction by ether. On shaking ether and water together each dissolves a little of the other. When the shaking is stopped the liquids separate into two layers, the ether being the uppermost. Suppose we are dealing with the aqueous solution of a substance that is more soluble in ether than in water, and that the solution in water is inconvenient to work with, the substance can be

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\* See note on p. 21.

almost completely removed as a solution in ether by shaking the solution repeatedly with small quantities of ether, which can then be removed by distillation.

In practice, the work lead is purified by remelting, to effect the removal of copper, arsenic, antimony, &c. The lead, so far purified, is then melted in a pot and heated to about 500 deg. C., lumps of zinc are added and the liquid is well stirred with iron paddles. The quantity of zinc added depends on the richness of the lead in silver, but in any case is very small and rarely exceeds 2 per cent. of the weight of the lead. When the agitation is stopped, the liquid is allowed to cool and a crust of zinc containing the silver solidifies on top of the still molten lead, is removed by ladles and liquated to separate some of the zinc. The remainder of the zinc-silver mixture is then transferred to graphite retorts and the zinc is distilled off. It is found to be advantageous in extraction by zinc—as in the case of ether—to add the zinc in three instalments, and not all at once. When the lead contains gold, about one-tenth of the zinc is put in at first, when the scum of zinc separated contains all the gold. The silver is then extracted by continuing the process. The remaining lead contains about 1 per cent. of zinc, which is removed by blowing air and steam through the molten metal, the zinc being blown away as oxide, leaving the lead in a very pure state. The Parkes process, now used extensively, has been rendered more efficient by the recent discovery that graphite retorts can be used for the distillation of the zinc.

These processes for desilverisation not only yield valuable quantities of silver but also produce lead in a high state of purity. In fact, lead as now produced is one of the purest of the commercial metals. It would probably not be so if no precious metal could be extracted from it, because in order to win the silver all other impurities must also be removed. Whereas work lead is hard, pure lead is soft and can be easily manipulated, purity being, moreover, very important in the starting material for the manufacture of white lead for making paint.

*Nickel* was discovered by Cronstedt in 1750. During recent years it has assumed an important position in the civilised world. It is malleable, ductile, hard, takes a high polish, and is very resistant to atmospheric oxidation. To these valuable properties nickel owes its use in the electroplating of small iron and steel articles to prevent rusting, in the manufacture of rifle bullets, which are covered with a layer of nickel to give a hard clean surface that will not foul the barrel, and also in the preparation of nickel steels and of certain alloys with copper and zinc, such as nickel silver, which are used in the manufacture of forks and spoons, ornamental articles, wire, medals, and coins. Nickel is also used in the finely divided state as a catalyst, in the hydrogenation of certain oils and fats. By the action of hydrogen in the presence of finely divided nickel, liquid oils such as fish oil, linseed oil, olive oil, can be "hardened" into solid fats suitable for the starting materials in the manufacture of foodstuffs, candles, and soap. For these purposes the nickel used must be very pure. The older methods of production were difficult and expensive, but in 1895 Ludwig Mond introduced a method by which the pure metal can be obtained at a comparatively low cost from the matte produced by the first smelting operation. Mond discovered that metallic nickel combines with carbon monoxide when heated to 80 deg. C. in an atmosphere of that gas, yielding a volatile compound, nickel carbonyl. The matte is roasted and then reduced at 400 deg. C. by producer gas. The reduced metal is then exposed at 80 deg. C. in a "volatiliser" to the action of carbon monoxide. The gas issuing from the volatiliser containing the nickel carbonyl is passed through vessels heated to 180 deg. C., where the nickel is deposited in the pure state. The carbon monoxide is obtained from flue gases by passing first through boiling potassium carbonate solution and then over hot coke. The carbon monoxide obtained by the decomposition of the nickel carbonyl at 180 deg. C. is also used over again. This brief survey shows how

Mond's scientific discovery and its exploitation has had its effect on very diverse industries.

*Sodium*.—Metallic sodium was first obtained by Sir Humphry Davy, in 1807, by the electrolysis of caustic soda, but no attempt was then made to manufacture sodium on the large scale by that process. Up to 1891 it was produced by carbon reduction methods. The method of Brunner, improved by Deville, consisted in igniting a mixture of sodium carbonate and charcoal; but this process was very wasteful and expensive, and the price of sodium was consequently high. In 1886 Castner employed caustic soda instead of sodium carbonate, and this improvement, the outcome of scientific research, effected substantial decrease in the cost of production. In 1891 the old process was entirely abandoned and replaced by Castner's electrolytic method, founded on Davy's discovery and developed in the laboratory, by which fused caustic soda was electrolysed in an iron vessel under special precautions for even heating and the maintenance of a constant temperature. The method was cleaner and more efficient, and as a result sodium became really a commercial product, thousands of tons being rendered available annually for the preparation of sodium cyanide for gold extraction, under the MacArthur-Forrest process for dealing with low grade ores and sand and slime tailings.

*Aluminium*—so much valued for its lightness, strength, and unalterability in air—has a history resembling that of sodium. It was first isolated in the pure state in 1827 by Wöhler by fusing the chloride of the metal with potassium in a closed crucible, and again by the same chemist by passing the vapour of aluminium chloride over potassium. In 1854 Bunsen used the method of electrolysis of the fused chloride, and Deville applied the method of Wöhler in attempts to manufacture the metal on a large scale using sodium instead of potassium. Samples of Deville's products were shown in ingots at the Paris Exhibition of 1855, where they occupied a prominent position, carefully guarded by gendarmes, only a few visitors being allowed to handle the exhibit, which was regarded as



a great curiosity. This was an incentive to further research, with the result that a short time later the large scale manufacture was established at Alais on the Loire. The use of sodium, then itself a costly metal, was only one item in the heavy expense involved. The method held its own for some years, but in 1887 Bernard Frères, of Paris, reverting to the method of Bunsen, founded their electrolytic process, using a mixture of cryolite and common salt as the electrolyte. Before 1887 aluminum was sold at £3 per pound. Now it can be made at very low cost, where power is cheap, to be sold at little more than a shilling per pound. The method whereby a solution of oxide of aluminium in fused cryolite is kept in the molten state, and decomposed, by an electric current, yields a metal of over 99 per cent. purity compared with the 97 to 98 per cent. metal from the older process. The expenditure of electrical energy is high, and in the light of our present knowledge it appears futile to endeavour to reduce it. When aluminium is used in the thermite process, an enormous quantity of energy is evolved in the form of heat, producing a very high temperature, the aluminium being converted into the oxide. To win back the metal from the oxide an equal amount of energy has to be put back, thus accounting for the quantity of energy absorbed in the preparation of the metal.

*Magnesium* was first isolated by Davy. It owes its method of preparation and present-day uses solely to scientific investigation. It is manufactured by a process similar to that used for aluminium, by the electrolysis of fused anhydrous carnallite, a double chloride of magnesium and potassium. The "magnalium" alloys of aluminium and magnesium are lighter than the former metal, give very good castings, and are as strong as brass and bronze. The use of magnesium in flashlight photography is well known.

*Molybdenum and Tungsten*, like aluminium and magnesium, are children of science. Both are used for making special steels, and tungsten is also formed

into filaments for incandescent electric lamps, its efficiency in this rôle being very great.

*Chromium*, which was discovered by Vauquelin in 1797, and is much used in the manufacture of special steels, has a very high melting point, and on that account cannot be prepared in a fused state by ordinary methods. The metal was isolated by Deville by heating chromium oxide and sugar charcoal in a lime crucible; and by Wöhler by heating the chloride with metallic zinc under a layer of sodium chloride, and subsequently removing the zinc by treatment with nitric acid, the chromium being thereby obtained in the form of a grey powder; but these and similar methods could not be adopted economically on a commercial scale. In 1893 Moissan published the method whereby a mixture of chromium oxide and carbon is heated to the high temperature of the electric furnace, giving a product containing large quantities of carbon from which it can be freed only by difficult and expensive processes. Ferrochrome, however, an alloy of iron containing 60 to 70 per cent. of chromium, is manufactured on a large scale by the thermite process. Chromite, an ore of chromium and iron, is finely crushed and well mixed with aluminium dust. The mixture is ignited with the aid of burning magnesium. The aluminium reduces the oxides of iron and chromium with evolution of great heat, and consequent production of a temperature sufficiently high to fuse the ferrochrome, the alloy being thus produced in a compact and homogeneous condition. Chromium metal of over 99.5 per cent. purity can be obtained by the thermite process, the principal impurities being small quantities of iron and silicon. The thermite process is used when freedom from carbon is desired, that of Moissan being applicable when the presence of a certain quantity of carbon is not objectionable.

*Thorium*, discovered by Berzelius in 1828, is interesting scientifically by reason of its radioactivity. It has found no useful application as a metal, but its oxide, thoria, has proved invaluable to the gas industry, being used for the manufacture of incan-

descent mantles, of which the world's production is estimated at over 400,000,000 annually. Thoria, when heated directly in a flame, possesses the property of converting heat energy into light. Research was therefore directed to the utilisation of this property, the evolution of the modern gas mantle being the result of purely scientific investigations, requiring great skill and patience. Not the least difficult problem to be solved was the production of thoria in the necessary state of purity. In the early history of the manufacture of the mantles, the known sources of thoria were not numerous, although the available ores were rich, and presented little difficulty in treatment, but the discovery of large deposits of monazite sand in South America stimulated the industry by considerably diminishing the cost of the materials employed. For a time, while the value of the sand remained unrecognised by the States wherein it was found, the sand was shipped to Europe as ballast—an illustration of the advantages to be gained from scientific investigation into natural resources. However, that is another story! Monazite is a complex mineral consisting of the phosphates of thorium and the metals of the rare earths, occurring mixed with other minerals as a sand. To obtain pure thoria from this ore a protracted treatment is necessary, involving concentration by tables and by magnetic separation, followed by fractional precipitation of the oxides from solution. The thoria appears on the market as nitrate. In the manufacture of mantles a cotton framework, supported on an asbestos collar, is soaked with a solution of the nitrate and dried; the cotton is burned away, and the resultant oxide is hardened by further heating, and stiffened by dipping into collodion, which in turn is removed by burning when the mantle is placed in position ready for use. It was found that the presence of about one per cent. of cerium oxide in the mantle increased to a maximum the transformation of heat energy into light, whereas a marked diminution of luminosity was observed when the quantity of cerium oxide was increased or diminished. For this reason the equivalent of one

per cent. of cerium oxide is added to the solution of thorium nitrate. The credit for practically the whole of the scientific work underlying the industry is due to Auer von Welsbach.

*Vanadium*, discovered in 1830 by Sefström, in the refinery slag of the iron ore of Taberg, in Sweden, is of increasing service to the maker of special steels. In effect 0.2 per cent. is equivalent to 3 to 4 per cent. of nickel, and experience tends to show that it imparts to steel the power of resisting changes caused by vibration, a most valuable property from the engineer's point of view. It is mainly used as an alloy, ferrovanadium, prepared by the thermite process. It is worthy of note, as affording an instance of the utilisation of "waste," that the mixture of metals obtained by reducing the rare earth oxides forming the residue of monazite after the extraction of thorium is employed, in the place of aluminium, to produce pure vanadium by a method resembling the thermite process.

#### THE NOBLE METALS.

*Gold*.—In the recovery of gold large quantities of metal were previously thrown away in tailings, owing to the fact that amalgamation left a certain amount unextracted from the ore. The Plattner chlorine method and the MacArthur-Forrest cyanide process have now rendered the tailing metal available. The Plattner method, which is also used in the treatment of auriferous pyrites, depends on the action of chlorine gas on the roasted ore, the chloride produced being subsequently leached out with water. The gold is then precipitated by treating the solution with some suitable material, such as ferrous sulphate, charcoal, sulphuretted hydrogen, sulphide of iron, or sulphide of copper. The MacArthur-Forrest process, also founded on the study of the chemical properties of gold, consists in the treatment of the sand or slime tailings from the amalgamation process, or, in some cases, a very low grade ore, with a dilute solution, not more than 0.3 per cent., of potassium or sodium cyanide, and the subsequent

precipitation of the dissolved gold by means of zinc shavings. The zinc is removed by distillation from graphite retorts, or sometimes by dissolution in sulphuric acid, the latter method yielding a somewhat richer bullion. In a method introduced by Tavener, the zinc-gold precipitate is mixed with litharge, sawdust and assay slags, and melted in a reverberatory, the resultant lead bullion being subsequently cupelled for recovery of the gold. In another method, devised by Siemens and Halske, the gold is precipitated from the cyanide solution by electrolysis, using iron anodes and lead cathodes and recovering the gold by cupelling the cathodes.

In the separation of gold from silver, nitric acid was at one time universally employed, but in 1802 D'Arcet utilised the fact, discovered in 1753 by Scheele, that concentrated sulphuric acid was equally suitable for the purpose. This constituted an improvement of considerable value, effecting a saving both of cost and time, and it must be remembered that in this connection "time is money," for gold brings interest.

*The Platinum Group.*—The metals of the platinum group are among the most valuable acquisitions of civilised man, and their availability is entirely due to chemists, among whom may be mentioned Achard, Janetty, Knight, Wollaston, Deville, and the firm of Johnson, Matthey and Co. Platinum itself is easily worked by the oxy-hydrogen flame method of Hare, modified and improved by Deville and Debray, and is useful for many purposes in which special resistant properties are essential, such as for vessels employed in analytical chemistry, for stills for the concentration of chamber acid, for standard weights and measures, for electrical leads fused into glass, as a catalyst in the contact process for making sulphuric acid, as a photographic medium, and for mounting jewellery.

Other members of the group are iridium, discovered by Tennant in 1804, used in combination with platinum in the construction of pyrometers, and as pure metal for tipping gold pens; osmium, discovered by Descotils in 1803, and by Tennant in 1804, used in the

preparation of metallic filaments of electric lamps, and combined with iridium for tipping gold pens and for the bearings of the mariner's compass; palladium discovered by Wollaston in 1803, employed by dentists and jewellers; and rhodium, discovered by Wollaston in 1804, used in the manufacture of certain forms of chemical apparatus.

NOTE (p. 12).—An alloy is termed eutectic when it is the most fusible of the alloys of two metals, the melting point being lower than that of either of the two metals of which it is composed. On cooling from the molten state it deposits a solid having the same composition as that of the molten mixture. For example, the melting points of lead and tin are 328 and 232 deg. Cent. respectively, but an alloy of these metals containing 31 per cent. of lead melts at 180 deg. Cent., any variation from this composition entailing a rise in the melting point. If an alloy richer in either constituent be slowly cooled, the metal present in excess of the above composition separates in the solid state as cooling progresses, until the composition of the remaining fluid is that of the eutectic, which then separates in the solid state. In the case of alloys of gold and silver there is no eutectic, the melting points rising regularly from that of silver to that of gold.

## CHAPTER II.

## HEAVY CHEMICALS AND ALKALI.

IN reviewing the progress made in chemical industries proper, we are met with such a condition of interdependence that it is impossible to avoid overlapping of the subjects to be treated. Moreover, the steps made in the improvement and development of processes, and in the evolution of new products, are so numerous that space will not allow of a comprehensive scheme. Indeed, the library of the Patent-office, one of the best for technological literature, cannot contain all that is due to chemists, nor disclose to which chemists the credit should be given for many important advances. We must, perforce, recognise, however, that science is the basis of all substantial development in the industrial arts, and that the rule of thumb is dead.

It has often been said that the prosperity of a country might be gauged by its output of sulphuric acid; yet it is remarkable how little the man in the street realises the importance of this substance. He has a vague idea that it is the same thing as, or in some way akin to, vitriol, which he knows is destructive to clothing, and is associated with charges of criminal assault wherein some evil-minded wretch has employed it as the agency for disfiguring the features of a fellow-being. If he were told that, even in normal times, the world's output exceeded 5,000,000 tons he would marvel how it is that he never sees, and probably never has seen, the substance. The reason for this is, that the consumer of large quantities of the acid generally finds it convenient and economical to make it himself. Thus, although large quantities are produced and consumed there is only a comparatively

small quantity on the market. When we come to consider its technical applications we find there is scarcely an industry that does not depend directly or indirectly on its use. It is employed in the manufacture of superphosphate fertiliser, as a solvent for metals—for example, in the parting of gold and silver—as a constituent of dipping baths for cleansing brass and bronze castings, and is used in the electrolytic refining of copper. Ammonia from the coal-tar and shale oil industries is absorbed in sulphuric acid, the resultant sulphate being extensively employed as a fertiliser. (The world's production of ammonium sulphate probably exceeds 1,500,000 tons.) The refining of oils, fats, and waxes, and of tar and petroleum products is also carried out with the aid of sulphuric acid, and it is extensively used in the manufacture and sulphonation of dyestuffs. Nitric acid, gun-cotton—and therefore, cordite, collodion and celluloid—nitroglycerine for dynamite, phenol, picric acid, T.N.T., ether, saccharine, many drugs, liquid glue, alum, persulphates, and a host of other useful substances are produced by processes in which sulphuric acid is an essential factor. It must be remembered, moreover, that many such substances are but the starting materials for the manufacture of other products; so that regarded as a mediæval ancestor, sulphuric acid can boast a genealogical tree of no mean order with many a noble family and innumerable progeny. Nor must we forget that not the least important of its uses is in the laboratory, where also many of its relations are to be found among the reagents required by the chemist. Discovered in the fifteenth century by the alchemists, it was made until about 1770 by two methods: (i.) by the distillation of crystallised sulphate of iron prepared by roasting iron pyrites; and (ii.) by the combustion of sulphur in a bell jar over water. Of these methods, the first survived until recently, being the only method available for making fuming acid, the second being the forerunner of the modern lead chamber process. Both are attributed to Basil Valentine (15th century),



who next discovered that by the addition of antimony sulphide and nitre, the yield could be substantially increased. Up to about the middle of the eighteenth century the principal workers at the problem had been alchemists—monks and others—the pioneers of modern science; and the only process that could be called a manufacture was that with sulphate of iron as starting material. At about that time, however, two French chemists, Lefèvre and Lemery, produced a method, used on a small manufacturing scale, wherein a mixture of sulphur and nitre, without antimony sulphide, was burned under a bell-jar over water. About 1770 Dr. Roebuck, of Birmingham, first employed lead chambers containing water, instead of glass bell-jars, thus considerably enlarging the scale of operations. The procedure was the same as in the bell-jar method. The floor of the lead chamber was covered with a few inches of water, and a kind of stand in the middle of the floor carried the charge of sulphur and nitre. The charge was ignited and the door was immediately closed and luted securely. The operations of charging, burning, and discharging were repeated until the acid attained the maximum strength compatible with the safety of the lead, when the liquid was drawn off and concentrated. This was a discontinuous process, but in principle it was the modern continuous method in a primitive state. The transition from the one to the other was gradual, the outcome of much thought and research. A step towards continuity of working was obtained by burning the sulphur in a separate vessel, and leading into the lead chamber the products of combustion, mixed with excess of air, and the fumes evolved on treating nitre with sulphuric acid. Complete continuity and greater speed of working was obtained when Kestner introduced the injection of steam into the chamber. The *rationale* of the process was explained by chemists by the aid of various theories, but a fact of great importance was clearly recognised, viz., that the nitric acid was merely a carrier of the atmospheric oxygen, and needed to be used only in small quantity.

Next it was found that the spent gas issuing from the chamber gave rise, in contact with atmospheric air, to oxidised nitrogen compounds that could be used again in the chamber. Nitre being the most expensive raw material, many efforts were directed towards the recovery of these gases and their return to the circuit. The most successful of these and the one universally adopted was due to the great French chemist, Gay-Lussac, the friendly rival in many fields of work of our own Sir Humphry Davy. The gases issuing from the chamber were conducted up a tower of lead or stone, packed with coke, down which a slow stream of strong sulphuric acid was caused to trickle. The acid issuing from the foot of the tower contained all the oxides of nitrogen present in the chamber gas. This acid was then conveyed to the top of another tower, invented by Glover, and in penetrating the length of the tower was met by the hot gases from the sulphur burners and deprived of its nitrogen oxides which were returned to the chamber with the ingoing gases, to play again their part in the transformation. The acid drawn from the chamber was concentrated in glass retorts, platinum being afterwards substituted for glass. Although the initial outlay on platinum was very considerable, the loss by breakage was avoided.

This short history of sulphuric acid manufacture should serve to illustrate how science has been the primary factor in its evolution. The subject of the use of iron pyrites as a source of sulphur will be deferred until we consider the alkali industry.

We must digress for a moment to refer to another industry in order to indicate the origin of the contact process. About thirty-six years ago, various methods were discovered for the preparation of artificial indigo, and endeavours were made to apply the best of these on a commercial scale to compete with the natural product. The starting material in the most successful processes was naphthalene, at one time regarded by the tar distiller as a nuisance but now recognised as a valuable product. In the

first stage of the synthesis of indigo, naphthalene is converted by oxidation into phthalic acid. This was originally effected by chlorination and subsequent oxidation with nitric acid; but the process was too expensive for successful application on the large scale. Next the discovery was made that the direct oxidation of naphthalene could easily be effected by fuming sulphuric acid in the presence of mercuric sulphate. At that time, however, the only method of preparing the fuming acid was the Nordhausen process, by heating sulphate of iron, and the product was too highly priced for the prospective indigo manufacturer. Cheap fuming acid was, therefore, a necessity. It had been known to chemists for a half a century or more that sulphuric acid anhydride could be made from sulphur dioxide and oxygen by passing the mixed gases over heated finely divided platinum, and it was found that by absorbing the anhydride in concentrated sulphuric acid the product was the fuming acid. In the laboratory, where the materials employed were comparatively pure, the method left nothing to be desired, but on the works where, for reasons of economy, materials of a crude nature, such as pyrites, had to be used, further obstacles were encountered. The process would go briskly for a time and then it would slow up and finally stop altogether. The platinum had lost its efficiency and the chemists were confronted with another difficulty. They are accustomed to this sort of thing and enjoy it. Indeed, some are almost disappointed when results come too easily and there is a lull in the chase. They found that the platinum had been "poisoned" by arsenic, antimony and mercury from the pyrites; they therefore devised the means for washing these oxides out of the sulphur dioxide, and with this purified material their labours were crowned with success. The manufacture of fuming acid and ordinary concentrated sulphuric acid by the "contact process" is a fast growing industry, and will doubtless in time largely replace the lead chamber process by reason of its efficiency and cleanliness, and the

compactness of the plant required. Moreover, it is convenient and economical to be able to produce acid of any strength without the expense involved in the concentration necessary in the older process. On account of the diversity of its uses sulphuric acid is required in varying conditions of purity and concentration, from the chamber acid and B.O.V. of commerce to the redistilled acid required in analytical operations. Researches have been conducted with a view to the elimination of impurities, and especially of arsenic. The contact process satisfies this requirement, but acid from the chamber process may contain this impurity in considerable quantity. The use of sulphur instead of pyrites results in the production of arsenic free acid, but chamber acid already containing arsenic can be freed from this impurity by precipitating it as sulphide with sulphuretted hydrogen before concentrating the acid. Another method has been suggested whereby dry hydrogen chloride is passed through strong sulphuric acid heated above 150 deg. Cent., when the arsenic is entirely removed as trichloride, but this has not received extensive application. Both these methods are founded on everyday laboratory experience.

One hundred and thirty years ago, as a result of the French revolutionary wars, France was cut off from the supply of alkali and an appeal was made to chemists "to render vain the efforts and hatred of despots," and, incidentally, to win a prize by producing a process for making alkali. This offer resulted, in 1794, in the submission to the Convention of more than a dozen processes, some of which had already been in operation, including that of the apothecary Leblanc, which was accepted. In 1814 it was introduced into England, and in 1823 the first works of importance were established near Liverpool by James Muspratt. In the Leblanc process sulphuric acid is employed for the decomposition of common salt. The resulting sulphate is heated with chalk and small coal in a reverberatory furnace; the mass is lixiviated with cold or tepid water; the

solution is evaporated to dryness and the product is calcined with sawdust in a suitable furnace. The soda-ash or crude sodium carbonate thus obtained is dissolved in hot water, treated with lime, to obtain caustic soda, to be used by the soap and candlemakers, or the solution of the carbonate in water is filtered and crystallised to give washing soda. We have indicated that the substances required for the process were salt, coal, chalk, and sulphuric acid. The first three were to be found in abundance in Nature, but up to that time sulphuric acid was comparatively expensive, and the demand for it was not such as to warrant its extensive manufacture. It was to meet the requirements of the Leblanc process that the output of the acid was enormously increased, and although the process has now been superseded by that of Solvay, as far as carbonate is concerned, and is being replaced by electrolytic methods for making caustic soda, it must not be overlooked that we owe to Leblanc, indirectly, our cheap sulphuric acid, and therefore a thousand and one other cheap commodities.

To return to the sodium carbonate, we may well ask how many good citizens and washerwomen who use it have any idea that a chemist has anything to do with its production? Possibly they think it exists naturally in the condition supplied; more probably still, they think nothing at all about it so long as it serves its purpose.

If the crystals are re-dissolved in water, filtered and re-crystallised, we have the pure sodium carbonate used in pharmacy. By passing carbonic acid gas into a cold solution of the carbonate, and by placing the crystals in an atmosphere of the gas, we obtain the bi-carbonate which is also employed in pharmacy, and as an ingredient of baking powders.

The aim of the technologist is to avoid waste of any kind, either of matter or energy, the cost of a product to the consumer being in a great degree dependent on the efficient utilisation both of raw material and of by-products. The alkali industry furnishes many examples. In the Leblanc process,

among the main products are soda ash, which we have shown is purified to obtain soda crystals, and "alkali waste," of which about 30 per cent. is calcium sulphide containing the sulphur from the original sulphuric acid. The waste was long regarded as useless, but is now treated for the recovery of the sulphur. Many attempts have been made to recover this sulphur in a useful form, but it was only comparatively recently that the Chance-Claus method was introduced, whereby the alkali waste is made into a paste with water, and acted on by carbonic acid gas—lime-kiln gas and furnace gas being used for the purpose. The sulphur of the calcium sulphide is converted thereby into sulphuretted hydrogen, which is mixed with a carefully regulated supply of air and burned in contact with hot ferric oxide in Claus kilns. The hydrogen burns off and the sulphur is deposited in a practically pure state—a very valuable product.

When, in 1839, an export embargo was placed on Sicilian sulphur, the alkali manufacturers, having to look elsewhere for their supply, found it in iron pyrites. The residue of oxide of iron from the pyrites burners was not used as a source of iron, as it retained enough sulphur to render it unfit for this purpose. The pyrites used also contained a certain amount of copper, averaging 3 per cent., as well as small quantities of gold and silver. Until 1865 these residues were dumped as useless, but in that year Henderson introduced a method whereby the whole of the copper could be recovered by roasting the residues with common salt, lixiviating the mass with water, and precipitating the copper from the resultant solution by means of scrap iron. In 1870, a method was devised by Claudet to recover the gold and silver occurring in the residues. The copper solution formed on lixiviation in Henderson's process contains the gold and silver as chlorides dissolved in the excess of common salt. By Claudet's method the gold and silver are precipitated by the addition of zinc iodide to this solution, the precipitated iodides being subsequently reduced with metallic zinc in the presence of hydrochloric acid.

Thus by the application of science the revenue of the sulphuric acid and alkali maker increased, the price of his products is lowered, and valuable materials are rescued from the dump. More than 500,000 tons of pyrites are burned annually in England for the sake of the sulphur. The residue from this yields on extraction about 15,000 tons of copper, 400,000 ounces of silver, and 2000 ounces of gold, the final residue being transformed into a valuable source of iron.

In connection with this subject can be related one of the most interesting episodes in industrial history. For some time after the inception of the Leblanc process, the hydrochloric acid produced was allowed to escape into the air, as no use had been found for it. Metal ware was corroded, and vegetable growth destroyed for miles around the works and the nuisance gave rise to much litigation. The obvious remedy was to absorb the noxious gas, and to effect this many of the larger works adopted in 1836 a method devised by Gossage. It was not until 1863, however, that the Alkali Act was passed, enacting that not less than 95 per cent. of the hydrochloric acid gas produced should be absorbed, a regulation rendered more stringent by subsequent legislation. Some idea of the quantity concerned may be gathered from the fact that at that time about 3000 tons of the gas were produced annually in England. To hark back to the earlier days when the makers first laid out capital to provide means for the absorption of the gas, they naturally wondered what return they could get for it. This was forthcoming in the increased demand for chlorine to make bleaching powder to be used for bleaching raw cotton and materials for paper making. Chlorine, set free from the hydrochloric acid by the action of manganese dioxide, was led over slaked lime, and the product was bleaching powder. The same gas passed into cold solutions of caustic soda and potash formed useful bleaching solutions, while if boiling potash was used the product was chlorate of potash, a valuable substance in pyrotechny, in the manufacture of

certain explosives, and in medicine. The manganese dioxide employed to liberate the chlorine was converted into a useless product, which was a loss to the manufacturer. Science again came to his aid in the discovery of Weldon, that the action of lime and air on the manganese waste resulted in the regeneration of an oxygenated body which might be used in exactly the same way as the original dioxide. Thus, by this process the dioxide acts merely as an agent in liberating the chlorine, and can be used over and over again, atmospheric oxygen being the real factor concerned in the change.

The Deacon process for the manufacture of chlorine from hydrochloric acid is a scientific method, whereby hydrochloric acid gas and air are passed over hot brick-work impregnated with copper salts. The products are chlorine gas and water, the copper salts acting merely as carriers of oxygen. The only losses are that of the hydrogen of the hydrochloric acid and the oxygen of the air.

The two processes last considered, together with the lead chamber sulphuric acid process, being among the earliest of this type to be employed, serve to show how the chemist is teaching the manufacturer to use catalytic and contact agents to effect certain chemical changes—more especially those involving oxidation. Such processes are numerous and successful at the present day, effecting wonderful economies, needing only simple and compact plant, and bringing about the required changes in the cleanest and least wasteful manner.

*The Ammonia-Soda or Solvay Process.*—In this process sodium bicarbonate is produced by the action of carbon dioxide on an ammoniacal solution of common salt. The bicarbonate crystallises out, leaving ammonium chloride in solution, the ammonia being recovered by heating the solution with lime, and used over again. The lime employed is burnt at the works, the lime-kiln gas being the source of some of the carbon dioxide, while the gas expelled from the bicarbonate by calcination to make normal carbonate provides the remainder. The salt solution



used—brine pumped up from brine pits—is subjected to preliminary purification. Magnesium salts are precipitated by the addition of lime, the lime salts being afterwards removed by adding the necessary quantity of sodium carbonate or ammonia liquor containing ammonium carbonate. After settling the solution is drawn off and is then ready for use.

This process, which was patented by Dyer and Hemming in 1838, though simple from the chemists' point of view, presented considerable mechanical difficulties. The first attempt to utilise the reaction on the large scale was made by Schloessing and Rolland in 1855, at a works near Paris. At the end of two years, however, the difficulties remained unsolved and the project was abandoned. In 1863, Solvay, who had taken out a patent two years earlier, erected an experimental factory near Brussels; as the result of perseverance, he secured the success of the process, and in 1872 established a far larger works near Nancy. Two years later the process was introduced into this country, under the Solvay patents, by Mond, continued by Brunner, Mond and Co., Limited, at Northwich, where for the first time natural brine was employed and other improvements were adopted. In 1895 the production by the Solvay process exceeded that by the Leblanc process, over which it has several incontestable advantages. The use of brine from the pits effected a great economy that could not be shared by the older process. The Solvay process is cleaner and the product purer. There is, of course, no sulphur to be recovered, but the chlorine from the salt is frequently wasted as calcium chloride. As an improvement in the process, magnesia is now used in some cases to liberate the ammonia from the mother liquor, the resulting magnesium chloride being subsequently decomposed by heat into magnesia (to be used over again) and hydrochloric acid.

Before leaving the subject of alkali we must note that electrolytic methods of manufacture form an increasingly important branch of the industry. Solutions of common salt are electrolysed in a special vessel, of which the Castner rocking cell is a type,

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and caustic soda and chlorine, both marketable products, are obtained in separate compartments. When the process is modified so that the chlorine is allowed to come into contact with the soda solution, chlorate or hypochlorite may be produced by employing hot or cold solutions respectively. The value of chlorates has already been indicated; sodium hypochlorite is used as a bleaching agent and as an ingredient in one step of the manufacture of indigo.

## CHAPTER III.

## COAL AND COAL GAS.

WE live in an age of coal and iron. The great war is waged very much with coal—or rather, what we get from it—and iron ; on the manipulation of these substances by engineers and chemists the production of munitions of war largely depends. Some of the coal we use to smelt the iron ore and to fashion the metal into convenient form for our use. When we have won the iron we can use it, scrap it, and use it again many times, but the coal once used is destroyed for all time. The world's annual production of this valuable mineral probably exceeds 1,335,000,000 short tons, and it is utilised (1) as a domestic fuel, with which we are all familiar ; (2) as a source of mechanical and electrical power through the agency of steam ; (3) as a reducing agent in certain chemical and metallurgical operations ; (4) for the production of coke in ovens ; (5) as a source of gas for illuminating and heating purposes and of many other valuable products.

The influence of scientific thought on the second of these uses is well known, though perhaps its extent is not always clearly recognised. For more than half-a-century, steam engines were designed to meet the requirements of coal as a fuel. It was the bed-rock of the art of engineering. The abundance of coal gave impetus to invention and the modern steam engine is the result of the co-operation of physicists, chemists and mathematicians, with the practical engineer. As a reducing agent in applied chemistry and metallurgy coal itself is less used than coke. The ironmaster is a great consumer of coke—oven coke as a reducing agent, and it has found an important use in the manufacture of water gas and producer gas.

The first, a mixture rich in hydrogen and carbon monoxide, is obtained by passing steam through red hot coke; the second, a mixture of carbon monoxide and atmospheric nitrogen is formed by the similar treatment of carbon dioxide produced by the combustion of coke. Although water gas has a much greater calorific power than producer gas, it is not economical to make it alone, because the reaction between the coke and the steam is endothermic and the coke chamber must be heated externally to maintain the requisite temperature. Dowson gas and Mond gas are mixtures intermediate between water gas and producer gas, made by combining the two processes and passing a mixture of steam and air over the red hot coke. When the coke cools during the operation the temperature is raised again by cutting off the steam and allowing air alone to pass through. The use of these gases for heating purposes is very economical and finds extensive application.

As one of the most striking examples of the influence of science in industry, coal gas manufacture demands consideration in somewhat fuller detail, treating of the distillation of a highly complex body from which the chemist has obtained a vast variety of useful substances. The history is interesting also as an illustration of a development of philosophical experiment. In the seventeenth century the pursuit of science was the hobby of many men of learning and particularly of the clergy. The Rev. Dr. Clayton, rector of Crofton, distilled gas from coal and collected it in a bladder; the fact being communicated, in 1688, to the Royal Society by Boyle. In 1750, Dr. Watson, Bishop of Llandaff, not only distilled gas but conveyed it in pipes from one place to another. The credit, however, is given to an engineer, William Murdock, for the first suggestion that coal gas should be generally employed for lighting purposes. In 1792 he conveyed it from iron retorts through tinned iron and copper pipes, tapped at intervals, a distance of 70ft., lighting his house and offices. His early experiments were carried out at Redruth, and six years later he lighted the Soho foundry of Boulton and

Watt, at Birmingham. In 1799, Le Bon commenced similar experiments in France. In 1807, after one side of Pall Mall had been lighted by Winsor, a Bill was promoted in Parliament to authorise a company for the supply of gas in London; in 1810 an Act was passed for this purpose, and two years later a charter of incorporation was granted to the Gas Light and Coke Company, still by far the largest gas undertaking in the world. Westminster Bridge and the Houses of Parliament were lighted in 1813, and from that time the practice of gas lighting spread rapidly in all civilised countries.

The gas industry is essentially chemical, though it was formerly entirely controlled by engineers. There was a time when gas engineers were disinclined to show much appreciation of the chemical aspects of the industry. In some works the chemists, if any were employed, were exclusively relegated to the laboratory for routine testing without any opportunity of acquiring experience in large scale operations. The remuneration and prospects of such chemists were so poor that few worthy of the name could be induced to remain long in such employment. In many important works, however, chemists acquired the essential knowledge of the engineering side of the industry, led the way in the introduction of improved methods and effected developments of a far-reaching character, especially in the profitable utilisation of material hitherto regarded as waste and the manufacture of new products.

Enormous quantities of coal are subjected to destructive distillation to obtain its numerous and valuable decomposition products, of which gas, tar, ammonia and its salts, coke, and gas carbon are made on a huge scale and all consumed. The gas provides light and heat, whilst the tar, useful in many ways in the crude state, gives, when distilled, benzene, toluene, solvent naphtha, carbolic acids, naphthalene, anthracene, and many other substances, which in their turn yield, in the hands of the technologist, a host of further useful bodies, including explosives, dyes, disinfectants, and drugs. Pitch, the residue of tar distillation, is

used largely in the manufacture of patent fuel and provides excellent material in road making. Ammonia is employed in medicine, in the laboratory, and in cleaning cloth, and there are many uses for its salts, especially the sulphate, a valuable fertiliser. Gas carbon, a hard, compact substance, is used by electrical engineers in the operation of arc lamps and furnaces, and as a fuel in making producer gas.

The purified coal-gas of commerce roughly consists of—hydrogen about 50 per cent. by volume, and marsh gas or carburetted hydrogen about 35 per cent., carbon monoxide 5 per cent., heavy hydrocarbons 5 per cent., and nitrogen 5 per cent. As it issues from the hydraulic mains, which receive the vapour from the ascension pipes from the retorts, it is not at once ready for delivery to the consumer. Besides its essential constituents, it contains substances such as condensable hydrocarbons, ammonia, carbon dioxide, carbon bisulphide, sulphuretted hydrogen, cyanogen, and cyanides, some of which are of sufficient value to pay for their extraction, all being undesirable impurities on account of their reducing the heating power of the gas or of the objectionable character of the products of their combustion. These bodies are therefore removed by condensation by cooling, "scrubbing" with water, and by passing the gas over suitable materials. The operation of scrubbing with water or with aqueous liquors from the hydraulic mains removes the ammonia and part of the carbon dioxide. The gas then passes into a chamber containing moist slaked lime, where cyanogen compounds and the remainder of the carbon dioxide are removed, the former in a state from which they cannot be recovered. Their recovery from the gas, however, can be effected, when desired, by a preliminary treatment with oxide of iron before the gas passes through the lime chambers.

After the lime treatment the gas is led over moist oxide of iron, or Weldon mud, for absorption of the sulphuretted hydrogen, the material when spent being revived by action of the air. The gas next passes over sulphided lime—the substance

formed by the action of sulphuretted hydrogen on slaked lime—to eliminate carbon bisulphide, and, finally, undergoes an extra check treatment with oxide of iron, or Weldon mud, to remove any traces of sulphuretted hydrogen taken up from the sulphided lime. Subject to passing the prescribed tests for illuminating and heating power, the gas now passes to the holder—in ordinary parlance the gasometer—and is ready for the public supply.

It is obvious that science is responsible for such a process of purification. There is scope for chemistry, physics, and mechanics in every step.

We have stated that the pipes from the retorts convey the vapour to the hydraulic main, where it is partially condensed, and the liquid thus condensing forms two layers, coal tar and aqueous liquor. The latter is uppermost, and contains ammonia and other soluble bodies. The tar was for long the bugbear of gas manufacture, its disposal being a difficult problem, but now it is of such value that the industry of tar distillation has grown to be of great importance. It is distilled in large iron stills, the vapours evolved from which are condensed, the distillate being separated into fractions as follows:—First runnings up to 105 deg. Cent.; light oil from 105 to 210 deg. Cent.; carbolic oil from 210 to 240 deg. Cent.; creosote oil from 240 to 270 deg. Cent.; anthracene oil from 270 up to the pitching point, this last temperature being determined by the quality of pitch desired. The first runnings form two layers in the receiver, consisting of ammoniacal liquor and crude naphtha. These are separated, the former being added to the bulk of ammoniacal liquor, the latter being reserved for subsequent treatment. The second or light oil fraction, consisting mainly of hydrocarbons of the benzene series, is first re-distilled, yielding first runnings, which are added to the crude naphtha from the original tar first runnings, and last runnings which are worked up with the carbolic oil.

The crude naphtha is washed with caustic soda solution to remove phenols in an easily recoverable form; then with strong sulphuric acid, which dis-

solves bases and unsaturated bodies, and carbonises other impurities, forming substances of a heavy, tarry nature, and finally another soda washing is given to remove the residual sulphuric acid. The spent sulphuric acid is used in the ammonia plant for the production of sulphate of ammonia. The naphtha so far purified is next redistilled from an iron still. Two fractions are collected—crude benzol up to 140 deg. Cent., and solvent naphtha from 140 to 170 deg. Cent., the residue in the still being reserved for addition to the carbolic oil. From the crude benzol are obtained by further acid and alkali washing and careful fractionation, forerunnings of benzol, containing benzene, toluene, carbon bisulphide and thiophenes, commercial and pure benzol and toluol, and solvent naphtha. Benzols and toluols are used by the dye manufacturers, and at the present day in enormous quantities in the manufacture of explosives, benzene being the starting point in one process for making picric acid, toluene being the material from which T.N.T. is made. Solvent naphtha is used as a solvent for india-rubber, the higher boiling portions containing naphthalene, forming a fuel for naphtha lamps.

The carbolic oil is treated by cooling to separate naphthalene, and subsequently washing with a solution of caustic soda, which dissolves the carbolic and cresylic acids. These acids are recovered by neutralising the solution with sulphuric acid, when crude carbolic acid and sodium sulphate are formed, the former being subsequently worked up for pure carbolic acid and cresylic acid, both used in the manufacture of dyes, disinfectants, and explosives. A modification of the above method is that known as the West-Knight and Gall process, whereby the oil is treated with a mixture of sodium sulphate solution and lime for the production of sodium "carbolate" and sulphate of lime. The solution is worked up as before, the sodium sulphate being utilised again for mixing with more lime. The insoluble oil is either mixed with the light oil or is worked up for naphthalene.



Creosote oil is of value as a source of naphthalene, and for preserving wood from the action of the weather and destructive insects. Naphthalene, once a waste product, is now used largely in the manufacture of dyes, being the parent substance of artificial indigo, as an insecticide, and in other minor rôles. Anthracene oil is the source of anthracene, a condensed hydrocarbon of the benzene series, from which the alizarin dyes are made.

## CHAPTER IV.

## DYES, EXPLOSIVES AND CELLULOSE.

THE invention of dyeing has been attributed to the Phœnicians, probably because it is chronicled that Solomon sent to Hiram of Tyre for "a man cunning to work" *inter alia* "in purple and crimson and blue." The Tyrian purple was derived from the throats of a species of murex, a molluscous animal, a single drop from each. Other dyes from animal substances include sepia derived from the black secretion of the cuttlefish, and cochineal which consists of dried female cochineal insects, discovered by the Spaniards in 1518.

The importance of the dye industry is not so much in the value of the dyes as in the vast interests of the textile industry with which it is so intimately associated. At a high estimate this country does not use annually dyes to the value of £2,000,000, or, say, less than 1s. per head, presuming the use to be confined to the British Isles; but the various industries affected exceed in annual value a sum of £200,000,000, and the labour involved in dyeing and printing processes is not far short of 2,000,000. Clearly then we cannot afford to be dependent on other countries for supplies of materials of this kind so long as we have the power to produce them ourselves. It is well known that the Government has now given active support to the industry; and we may rejoice that British Dyes, Limited, and other British dye concerns are making good progress towards its firmer establishment. Even before the outbreak of war, progress had been made in certain directions towards successful competition with the Germans, and since the war, by the aid of science, discoveries have been made which, in the view of the enemy producers, were calculated to

defy our chemists for at least ten years. Compared with the period occupied by the Germans in discovering artificial indigo—about thirty-five years and an expenditure of over £1,000,000—the taunt may be taken as a compliment; but in two years from the discovery of artificial indigo 426,100 out of 755,900 acres of plantations went out of cultivation. It was first sold in 1897 and in the course of a few years drove the natural dyestuff out of the markets of the world, being only about one-third of the price, and the business passed from India to Germany.

The history of the subject covering the consideration of all the dyes known would fill volumes exceeding in bulk the "Encyclopædia Britannica." The number of dyes revealed by science and the substances which science can foretell with certainty would form dyes, and the myriad derivatives of known colouring matters, would run into many thousands, though 800 to 1000 should be more than sufficient for all practical purposes.

The artificial dyes have several advantages over natural products. The range of shade for any colour can be extended and graded by the employment of suitable materials in a manner that cannot be attained by using the natural dyes; the purity of artificial dyes is much greater, and the total cost of production is considerably less. On account of this superiority of synthetic dyes, the cultivation of indigo and madder, and the trade in cochineal have been almost completely overshadowed. Both indigo and madder have been investigated by scientific men, and the composition and nature of the dyestuffs determined. Further researches have led to the discovery of methods of synthesis of these substances, not only interesting from an academic point of view, but capable of holding their own and beating their natural prototypes in commercial competition. The use of cochineal has been largely replaced by the discovery and utilisation of azo-red dyes which imitate the colour very closely, such, for example, as Bieberich scarlet. The most important material used in the economical manufacture of indigo is naphthalene obtained from the

creosote oil fraction of the tar distiller by cooling, washing the crystals produced with alkali and with acid, and distilling or subliming the product. Other ingredients are chloracetic acid and sodium hypochlorite, the preparation of which provides one of the numerous outlets for the elementary chlorine of the alkali manufacturer. A short sketch of the method of Heumann will not be out of place.

Naphthalene is converted into phthalic anhydride by heating with sulphuric acid and mercuric sulphate. The phthalic anhydride in turn is transformed into phthalimide by heating under pressure with ammonia. By the action of sodium hypochlorite on phthalimide, anthranilic acid is produced and this substance, when treated with chloracetic acid, yields phenyl glycine-carboxylic acid, which by fusing with alkali, dissolving the melt in water and passing a stream of air through the solution, yields indigo blue. This complex series of operations has met with complete commercial success.

Alizarin, the dyestuff contained in madder, is made from anthracene, another coal tar product, by the action of sodium bichromate and sulphuric acid to form anthraquinone; this is transformed by the action of sulphuric acid into anthraquinone sulphonic acid, the sodium salt of which when fused with soda and a little potassium chlorate yields a compound of alizarin containing sodium, from which alizarin itself is made by the action of acid.

Bieberich scarlet, one of the naphthol azo dyes, a very important group, is, like indigo, prepared from naphthalene as starting material.

These three examples serve to show how the laboratory and the factory have replaced the cultivation field. There are also thousands of new dyes prepared from benzene, toluene, and carbolic acid, as well as many others from naphthalene. The name "coal tar dyes," however, is rather misleading to the uninitiated, for it seems to imply that the dyes exist as such in the tar and only need extraction. What is meant, is that the raw materials are found in the tar and need to be transformed before anything of the nature of a dye can be produced.

The recovery and utilisation of these tar products in the manner indicated is a great achievement. The first known coal tar colour mauveine was made from aniline by Perkin in 1856, aniline having been discovered by Unverdorben, thirty years earlier, by distilling indigo.

*Dyeing.*—The processes of dyeing and calico printing are definitely chemical and depend entirely on scientific control. Dyes are transparent and the effects they produce vary according to the light reflected by the fibres of materials before they are dyed. Obviously, therefore, black cannot be dyed, and such colours as red, blue, and yellow can only be dyed in the same hues, unless the material, as is possible in the case of velvets and velveteens, be previously bleached. White reflects all rays and is essential as the basis for bright dyes. There must be chemical combination between the colouring matter and the cloth, and the dye must be dissolved in a solution having a weaker affinity for the colour than the cloth, while for economical working there must be accurate adjustment between these relations. Wool has a stronger affinity for dyes than silk, cotton, or linen. The solutions used must be varied as occasion requires. The choice of dyes for a given material involves the consideration of fastness to washing, and the action of light. Certain dyes will fix themselves directly to certain fibres but not to others without the use of mordants. The mordants commonly employed, such as tannin, and the oxides of iron and aluminium, were discovered empirically, but science has explained their action, while research has contributed to the discovery of many new kinds of colouring matter. In the art of dyeing the neglect of science is mainly responsible for the loss incurred by spoiled and impoverished material.

#### EXPLOSIVES.

From a brief review of one of the most interesting arts of peace we will pass to one of the principal industries of war. The methods of production of explosives are so closely allied to those of the coal

tar dyes that without much modification of plant the dye maker can turn his attention to the war industry. We will not go so far as to suggest that the development of the dye industry of the Germans was part of their plan of preparations for war, but they have undoubtedly been able to take advantage of the existence of their great factories for fine chemicals and dyes in this connection. From the discovery of *pulvis fulminans* by Roger Bacon in the thirteenth century, the invention of gunpowder and guns by Swartz, the monk of Cologne, in the fourteenth, and the first use of cannon in ships in the sixteenth century, there was little development in the science or industry of explosives until the nineteenth century; then, of course, the need for explosives in mining and engineering was far in excess of that for war. Our present business is not to moralise, but to indicate with caution what science has done for an industry, the foundation of which lies in the realisation, by scientific men, of the causes of explosion. An explosive compound or mixture is one that can be converted exothermically and with great rapidity into gaseous products which at the high temperature attained would occupy at ordinary pressure a much greater space than that occupied by the original compound or mixture. The enormous pressure generated by sudden expansion constitutes the explosive force, and the principle involved has led to the utilisation of the explosive nature of a number of substances possessing this property which might otherwise have been overlooked. For instance, it is not at all easy to bring about the explosion of trinitrotoluene, or T.N.T. It is a relatively stable substance; but a study of its nature and comparison with picric acid, a similarly constituted body of known explosive properties, would lead one to suppose that it could be detonated by percussion.

In 1832, Braconnot demonstrated the formation of an explosive substance by the action of nitric acid on wood fibre, and in 1845 Schönbein obtained gun-cotton by treating cotton with a mixture of sulphuric and nitric acids. Its manufacture, however,

though started in several foreign countries, was not successful, the production being unstable and dangerous, owing to lack of care in the details of the operations involved. Sir Frederick Abel showed not only that must the starting material, cotton waste, be carefully selected, but that thorough water washing after nitration was an important factor. The instability of the Schönbein material was due to the presence of free acids. The introduction of centrifugal driers and of paper pulping machines for breaking up the cotton fibre facilitated the washing process, and reduced the risk of manufacture.

Gun-cotton is used for a variety of military purposes, such as filling subterranean and submarine mines and torpedoes, and it possesses the great advantage that it can be exploded when wet, although the wet substance is safe for handling, transportation, and storage. When dry, it is exploded by a primer of fulminate of mercury; when wet, a primer of dry gun-cotton is used. The explosive power of gun-cotton led to attempts being made to use it as a propellant, but gun-cotton, as such, is not suitable for the purpose because its explosion is very rapid, violent, and uncertain. Attempts to "tame" it by gelatinisation with certain organic liquids met with success in the smokeless powders of Walter F. Reid and Vieille. The most remarkable result in this direction, however, was achieved by Alfred Nobel, who produced a homogeneous mixture of gun-cotton and nitroglycerine by the evaporation of a solution of those substances in acetone. By the modern development of this method, gun-cotton, nitroglycerine, and a small quantity of mineral jelly are mixed well with acetone, and the resulting paste is squeezed through jets to form continuous cords, which, when dry, have the appearance of catgut. This is cordite, the propellant explosive used in firearms of many sorts and sizes.

Nitroglycerine, mentioned above, was discovered by Sobrero, in 1847, but its explosive properties were not utilised until its value was recognised by

Nobel. It is a fairly heavy oily liquid, detonating violently by percussion, when struck a sharp blow, or suddenly heated. On account of these propensities the substance, as such, is seldom, if ever, employed at the present time, but is converted into a safer form by incorporation with some inert material, as, for example, magnesia alba, or kieselghur, the product in the latter case being dynamite. In this form, although a certain amount of danger still attends its use, it is much safer than in the free state. Sometimes nitroglycerine is incorporated with an explosive diluent, as with collodion cotton, to produce blasting gelatine, a body with explosive power exceeding that of nitroglycerine; while a mixture of thinly gelatinised nitroglycerine with nitre, woodmeal, and a trace of soda, gives us gelatine dynamite, another useful blasting agent. Explosives of this class, used largely in mining, quarrying, and civil engineering operations, have been specially developed by Nobel's Explosives Company.

When we come to consider the class of substances used for the bursting charge of shells, it is difficult to give any individual the credit for their first application, or, shall we say, "give the devil his due." Picric acid, the oldest of these, was discovered in 1799 by Welter, and its nature as a derivative of phenol was elucidated by Laurent in 1842. Preparations of picric acid are used by various countries, as a military high explosive under such names as lyddite, shimose, and melinite. Its great disadvantage is that it forms very sensitive and highly explosive salts when left in contact with metals for any length of time. This drawback is not shared by T.N.T., which has come so much into use during the war. The substitution of T.N.T. involves a loss of explosive power, but this is more than counterbalanced by the advantages gained. It is used both alone and in conjunction with other substances such as aluminium powder and ammonium nitrate. Such a mixture is ammonal, a safe but very powerful explosive employed by the Austrians. Another very violent explosive is tetra-nitroaniline, discovered by Fleursheim. It is not



very largely used, as the materials required for its manufacture are comparatively expensive.

The whole industry is based on science, and should be controlled by trained men of science in every department. It has demanded its toll of human life, in spite of extraordinary precautions; but without science that toll would have been far greater, and certain it is that without the search for knowledge, the desire to experiment, and the power to apply the knowledge gained, such an industry could not exist.

#### CELLULOSE.

*Cellulose.*—Cellulose belongs to the class of substances known chemically as carbohydrates. All carbohydrates consist of carbon, hydrogen, and oxygen, the second and last occurring in the same proportions as in water.

Cellulose is not affected by ordinary solvents, but is attacked by strong sulphuric acid, yielding a starch-like body called amyloid, and is dissolved by ammoniacal solutions of copper salts, from which it can be precipitated in an amorphous form by the addition of acids. This property constitutes the basis of one method of making artificial silk. It may be mentioned, incidentally, that when heated to 200–220 deg. Cent. with caustic potash, cellulose is broken down into oxalic acid, and large quantities of that acid are made in this way. Sawdust is fused with potash in iron pans; the melt when cold is extracted with water, and the oxalic acid is precipitated as the insoluble calcium salt from which it is subsequently liberated by the action of sulphuric acid. This process, which was discovered by Gay-Lussac in 1829, and was first employed on the manufacturing scale by Dale in 1856, is far cheaper than the older method of oxidising sugar or starch with nitric acid.

The cellulose industry is held to include the manufacture of cotton, linen, paper and pasteboard, and hemp and jute articles. We do not claim much in the way of debts to science in connection with the

manufacture of cotton and linen. but will choose paper and pasteboard for our purpose, and then refer briefly to artificial silk and celluloid.

*Paper* may be regarded as one of the civilising agents in the existence of man. It is difficult to imagine what progress the world would have made without it. The early history of paper is obscured by conflicting records. It is believed to have been used in China long before the Greeks and Romans ceased to use papyrus, but according to M. Terentius Varro, a voluminous writer contemporary with Cicero, the invention was devised at Alexandria on the conquest of Egypt by Alexander the Great (B.C. 331). It was in use in Arabia over 1000 years ago, and the Crusaders are said to have brought the industry to Europe. The earliest MS. on cotton paper in the Bodleian Collection in the British Museum is dated 1049, while one on the same material in the Library of Paris is dated 1050. Paper made of linen rags was in use here in 1170. The Moors are credited with having introduced the industry into Spain, where 12th century specimens still exist. The first paper mill in this country was established by Tate, in Hertfordshire, in the reign of Henry VII., who visited it, and the first important one was started at Dartford, in Kent, in 1588, or thereabouts, when Queen Elizabeth granted a monopoly; for gathering rags and making paper, to Spielmann, the Court Jeweller.

Until the end of the 18th century paper was made by tearing and beating rags to pulp in a machine, dipping a wire sieve into the pulp, transferring the mass to a felt and pressing it in moulds of various sizes. About 1800 a Frenchman devised a method of making it in a continuous web, which he introduced into England, where it was steadily improved until about 1860, by which time, for all ordinary purposes, it had superseded the old hand-made method, although the latter is still employed for bank notes, bonds, ledgers, and important documents.

With the introduction of machine-made papers

the output has been vastly increased, the cost reduced, and the variety extended to such a degree that there are now probably more than 20,000 kinds. In 1820 the machines produced paper at the rate of about 40ft. per minute; the most modern can now exceed 500ft. per minute. Before 1860, paper consisted almost entirely of rags, but about that time an Englishman introduced the use of esparto, *Macrochloa* (or *Stipa*) *tenacissima*, a grass also employed for making mats, nets, baskets, &c., of which the consumption in paper-making is normally about 200,000 tons a year, at £4 to £4 10s. per ton, almost all of it coming to this country for the production of fine printing papers. Over 400 different materials have been tried in the industry, but rags and esparto are the chief for good papers. Since the year 1880, chemical wood pulp has been used as the chief material for middling kinds, and more recently mechanical wood—made by crushing wood between rollers or by pressing it against a grindstone—mixed with varying quantities of chemical wood pulp, has been employed for the cheapest newspapers and common printings.

Science has played an important part in the development of the paper industry. The introduction of cheap bleaching agents such as chloride of lime to which, as a by-product of the Leblanc process we have already referred, has effected considerable improvements and economies, while the utilisation of esparto and wood has been made practicable only by scientific research, the processes evolved from which we will now outline.

Wood fibre is a lignocellulose, a compound of cellulose and a complex substance called lignone, which acts apparently as a binding material. The forest wood is deprived of its bark and cut across the grain into small chips, which are cleaned and then boiled at high temperature, under pressure, in a solution of caustic soda. From coniferous wood the yield of cellulose is about one-third of the weight of the prepared wood treated, the other two-thirds being taken up by the alkaline solution. The caustic soda required, amounting to about 20 per cent. of

the weight of the wood, is recovered by evaporating the spent liquor, incinerating the residue and treating a solution of the ash with lime. The organic matter in the residue, on burning, provides a good deal of the heat necessary for evaporating the solution. The process, however, has one disadvantage in the fact that a proportion of the cellulose is destroyed by the action of the strong alkali. In order to obtain better yields two modifications have been introduced comparatively recently. One consists in the substitution of sodium sulphide for the caustic soda, the sulphide being prepared on the spot by the reduction of sulphate of soda with the residue obtained by evaporating the spent alkali. The cycle of operations is then completed by making up the working loss of sodium sulphide by the addition of sulphate of soda to the residue before incineration. The other modification consists in the application of an acid hydrolysing agent instead of the alkali. The acid substance employed is a solution of calcium or magnesium bisulphite containing approximately 4 per cent. of sulphur dioxide. This solution is prepared by passing pyrites gases up a tower filled with calcite or dolomite down which water is trickling. The cost of the process is slightly higher, but not out of proportion to the increased yield of cellulose.

The cellulose obtained by either of the methods is mashed to a pulp, washed free from adhering liquor, and bleached with chloride of lime and sulphuric acid, before being utilised in the manufacture of paper. Those who are interested in this subject may be invited to study the series of articles on "Paper Making," which appeared in Vol. CXX. of THE ENGINEER.

"*Artificial Silk.*"—The production from cellulose of materials resembling silk is the result of many years of scientific research and costly experiment. In 1889 the Comte de Chardonnet produced the first artificial silk by nitrating cellulose and dissolving the resulting product in a mixture of alcohol and ether, thereby obtaining a viscous liquid which he forced through holes of very small diameter into water.

The threads thus produced were then subjected to the reducing action of ammonium sulphide and converted into an amorphous cellulose having the appearance of silk.

The method now extensively used is that devised by Cross and Bevan, who have contributed largely to the existing knowledge of the chemistry and technology of cellulose. The starting material, wood pulp, is treated successively with caustic soda solution and carbon bisulphide, the viscous mass thus obtained being forced through small apertures, from which are produced filaments which are spun into a fine material also closely resembling silk.

*Celluloid*—a very useful substitute for horn, tortoiseshell, ivory, &c.—was first made in 1869 by treating nitrocellulose with campher and alcohol. Its inflammability, however, has proved to be a very serious drawback, attempts to overcome which have met with some success. By the substitution of acetate of cellulose for cellulose itself in the process, a non-inflammable product—*cellon* or *cellon*—is formed which for some purposes is more useful than celluloid.



## CHAPTER V.

## OILS, FATS AND WAXES.

OILS may be divided into: (a) animal, including whale and fish oils, stearin, which is mainly obtained from beef and mutton suet, and neats-foot oil from the feet of cattle; (b) vegetable, such as olive, linseed, cotton seed, maize, palm, rape, castor, and turpentine, and essential oils; and (c) mineral oils, so-called, such as petroleum, ozokerite, and shale. It is difficult to make a sharp division, however, for the reason that some are obtained from more than one of these sources; for instance, stearin exists in the vegetable kingdom, and petroleum is certainly derived from the products of long submerged fish life. The tar oils we have already noticed in dealing with coal and coal gas. Among the most useful substances at our disposal oils are employed as fuel, illuminants and lubricants, and provide us with material for food and medicine, as well as for the manufacture of paints and varnishes, polishes and perfumes.

Oil has been defined as a neutral fatty substance, liquid at ordinary temperatures; but although we are not satisfied with the definition, we will not attempt to improve upon it, preferring rather to proceed with our task of indicating the influence of science in the vast field of industry involved. That influence has been more marked in the direction of improvement and adaptation rather than of new and striking discovery. In some cases, however, scientific principles have been applied to the fundamental processes of oil production, with the result that substances at one time ignored as valueless have become the source of products now regarded as indispensable, while the science of geology has rendered inestimable service in locating and surveying sources of mineral oil; indeed,

a knowledge of economic geology is essential to all mining engineers.

The world's output of petroleum before the war was probably not far short of 350,000,000 barrels of 42 gallons, of which about two-thirds were produced in the United States. Dame Nature seems anxious to get rid of it as if it were the offensive exudation of a deep-seated abscess. If nothing could be profitably extracted from it we might well wish it to remain in the bowels of the earth, counting it nothing but a nuisance when it came to the surface. Science can at least claim to have made it useful, seeing that by the process of fractional distillation this disagreeable natural substance can be made to yield in enormous quantities such valuable products as illuminating gas, motor spirit, cleaning spirit, kerosene or lamp oil, paraffin wax, vaseline, and a viscid residue used as fuel. The crude petroleum itself would be useless for any of the purposes to which its derivatives are applied, mainly on account of its highly volatile constituents, which are a source of danger in transport and storage, owing to the inflammable nature of the vapour arising from it. The crude oil is conveyed by pipe lines, in some cases over a distance of several hundred miles, to the refinery, where it is distilled into temperature fractions. The lighter fractions are purified by washing with sulphuric acid, alkali and water; while sulphur, when it occurs in objectionable quantity, must be removed by means of copper oxide. Among the higher fractions lubricating oil is purified by filtration through animal charcoal.

The lightest fraction, cymogene, which requires special cooling and pressure for its condensation, is used in ice-making machines. Other fractions obtained are rhigolene, the illuminant used in the pentane standard lamp, and as a local anæsthetic in surgery; gasolene, employed for the carburation of water gas for illuminating purposes, for making "air gas," and as a solvent; ligroin, also a solvent; benzine or petrol, which supplies us with motor spirit; and kerosene or lamp oil. Among other products may be mentioned paraffin wax, which, with an admixture of stearic

acid, is used for the manufacture of candles, solar oils, various grades of lubricants, and vaseline. The quantity of lighter fractions can be increased if desired by the "cracking" of the more complex bodies.

Astatki, the residue from the distillation of Russian petroleum, yields, on distillation, an excellent illuminating gas, besides quantities of benzol, toluol, naphthalene, anthracene, and pitch.

The shale oil industry, founded by James Young, of Kelly, in 1851, which produces valuable quantities of illuminating and lubricating oils, ammonia, and paraffin wax, depends in a similar manner on scientific operations.

We claim less for science in the extraction of animal and vegetable oils, which has been practised since time immemorial, but must place to the credit side of the account the responsibility for the differentiation and classification of such oils, the selection of their most useful applications, with methods of purification and of analysis and valuation.

Vegetable oils, such as linseed oil—a so-called drying oil—and turpentine are used as vehicles in the manufacture of paints and oil varnishes. The paint industry has derived great benefit from science in the discovery and application of new pigments, and in the improvement of the older methods of making pigments. Turpentine is the starting material for the manufacture of artificial camphor, a synthesis that is a credit to organic chemistry, and although the artificial product cannot as yet be made to compete with the natural substance, it renders good service in keeping down the price of natural camphor, of which the production is practically monopolised by the Japanese. Other vegetable oils, such as olive oil, rape oil, maize oil, and castor oil, are employed as lubricants, whilst some are good illuminating oils.

The essential oils, of which oil of turpentine is an example, are vegetable oils used in many cases as perfumes. There are three methods of winning the essential oils: (1) by distillation with steam; (2) by pressure of the plant substance and (3) by extraction



with suitable solvents. Science has entered largely into the essential oil industry by finding the constitution of many of the odoriferous principles, which have afterwards been successfully made in the laboratory from simple materials. In some cases, where the actual substances have not been made, very close imitations have successfully competed with the natural products. Examples of the first are terpinol, which is the important constituent of Lily of the Valley, and coumarin, New Mown Hay and Jockey Club; whilst in the second class we have such substances as ionone and nitrobenzene substitutes for essence of violets and oil of bitter almonds respectively.

#### SOAP AND CANDLES.

The soap and candle industries must now be regarded as offshoots of the oil industries. Their origin is remote, but it was not until 1813, when Chevreul published his remarkable researches on the composition of oils and fats, that anything was known of the true nature of the processes involved in their manufacture. Nowadays the chemist should be in paramount control of their production. The recovery of glycerine, which at one time flowed into our rivers and streams as a waste product, was a scientific achievement of far-reaching importance, as we have indicated in our remarks on explosives, while its use in medicine is considerable. Incidentally we may mention also that glycerine, mixed with water, prevents evaporation and freezing, and this property finds application in the mechanism of gas meters.

Both animal and vegetable oils are used in the manufacture of soap and candles. When fats and oils—such as tallow, palm oil, olive oil—are boiled in large cast iron pans with caustic alkali, they become decomposed and yield an alkaline salt of the fatty acid—soap and glycerine. The excess of alkali and the glycerine are separated by the addition of a solution of common salt; the soap, being insoluble in the brine, rises to the top, and is ladled out as a granular curdy mass, run off into frames—boxes—to cool and solidify. Hard soaps, such as curd and yellow soap, are compounds

with soda, consisting of about 26 per cent. of water, 7 per cent. of soda, and 66 per cent. of fatty acids, with, in the case of yellow soap, a small percentage of resin. Soft soaps are compounds with potash, or potash and soda, with fatty acids derived from drying oils, such as whale and seal oils, linseed, &c. With regard to the water content of hard soap it has been rumoured that, since soaps containing as much as 90 per cent. of water have been encountered, it appears to be the aim of some soap makers to cause water to stand upright.

#### CANDLES.

The old tallow dips, prepared by dipping a wick repeatedly into melted tallow, gave rise, on burning, to a pungent substance called acrolein, produced by the decomposition of the glycerine combined in the tallow. Modern candles are without this disadvantage, as they contain no glycerine, the free fatty acids from which they are made being liberated from the fat either by the hydrolytic action of sulphuric acid, or by precipitation of the lime salt and its subsequent decomposition with sulphuric acid. The fatty acid—*e.g.*, stearic or palmitic acid—so prepared is melted and cast round about wicks in moulds of pewter or tin, or sometimes of glass, supported in a wooden frame, the upper part forming a trough. The wicks are arranged taut, the wax is poured in, cooled with water to solidification, and removed as candles. All sorts of waste fats, such as those from wool washing and glue making, are used for making candles, the free acid being extracted by treating the fat with sulphuric acid.

These industries furnish examples of the utilisation of waste products. The soap used for cleansing purposes in yarn mills is recovered by precipitating the soap from waste liquids with lime, and pressing the precipitate into briquettes, from which sufficient gas can be obtained by distillation to light the mills. Efforts are at the present time being made to recover fat from sewage, mainly for the sake of the glycerine content.

## EDIBLE FATS.

The invention of butter substitutes, now popularised by prevailing conditions and the need for the exercise of economy, is due to the chemist. These substances are commonly made by mixing intimately a solid animal fat, such as stearin, with some vegetable oil, such as cotton seed or cocoanut oil, and milk. The use of solid animal oil for this purpose absorbs some of the raw material formerly available to the soap maker, but the deficiency has been made good by the conversion of the plentiful supply of vegetable oils, such as olive oil, into solid fats by hydrogenation in the presence of finely divided nickel, to which we referred in dealing with that metal.

## CHAPTER VI.

## LEATHER.

UP to the close of the eighteenth century the progress of industry was slow but sure, much of it based undoubtedly on the workings of great minds and patient inventive genius, and much again on chance discovery; but the nineteenth century marked an epoch of development, definitely hastened by the advance made simultaneously in mechanical, physical, chemical, and biological science. Yet when we consider all that was done in ancient times, for example, in the winning of metals, in the dyeing of fabrics, in agriculture and the domestic arts, we are forced to marvel at the vast amount of knowledge and experience, commonly referred to as empiricism, accumulated for centuries before the advent of modern science. We are also convinced that there is no finality in the matter, and that what appears to be ideal to-day will be improved upon to-morrow or the day after.

An ancient industry is the manufacture of leather, which had seemingly reached the highest degree of efficiency centuries ago if one may judge by existing specimens. To the modern chemist, however, the subject is open to further investigation, involving problems directed to the speeding up of production and decrease of cost without diminishing the quality—aims not easily attained, as many have learned from personal experience. In fact, one of our leading authorities has recently expressed the opinion that the science of this important industry is but in its infancy. We are reassured, however, by the statement that the work of Professor H. R. Procter and the Leather Department of the University of Leeds, was largely the factor which rendered it possible for the

nation to supply the enormously increased demand for the military equipment of the Allied Armies, including boots, belts, leggings, saddlery, traces, dressed sheep skins, and numerous minor requirements, besides the driving belts of the munition factories. With such a demand to meet, the price for the time being of leather for furniture, port-manteaux, gloves, book-binding, and parchment is naturally high.

The processes whereby raw hides are converted into useful and durable materials by treatment with various solutions of substances of animal, vegetable and sometimes mineral origin, are distinctly chemical and biological. They are investigated and explained by research, and modified and superseded by better processes, so far as the increase of knowledge admits, while accidental impurities of a harmful nature in the liquors employed can be traced and their presence avoided.

The hydrochloric acid washing given to hides that have been unhaired by lime, to free them from that substance, is clearly an operation of a scientific nature, and is also the chemical investigation of the water supply, the quality of the water being important. The science of bacteriology has rendered invaluable assistance in furthering our knowledge of puering—the process of softening hides prior to tanning. The changes involved in the old process of treating the unhaired and washed hides with an infusion of dog-dung have been investigated very thoroughly by scientific methods, and have been shown to be the result of bacterial action. Patents, founded on this knowledge, have been taken out for the use of artificial cultures of bacteria instead of the obnoxious infusion referred to. Some of these methods give excellent results, and would doubtless be more generally adopted were it not for the conservatism of the workman and his dislike of the trouble necessitated by a change of procedure.

The oldest method of treating skin and hide for the purpose of preservation in a flexible state, which consisted in kneading with fatty substances, is of

historic interest only, though chamois leather is still prepared with oil. Next in chronological order comes vegetable tanning, still very extensively used, the tanning liquor being an infusion of some bark, *e.g.*, of oak or willow. Up to the end of the eighteenth century the prepared hides were simply soaked in a strong infusion of the tan, but about that time Seguin, a Frenchman, introduced a method for soaking the hides successively in tan liquor, or ooze, of increasing strength, the untanned hide going first into the weakest, the completely tanned material being taken from the strongest liquor. By this means thorough permeation by the tan liquor was ensured, and the quality of leather considerably improved. This method was patented in England by William Desmond in 1795.

Sir Humphry Davy investigated the process of tanning with useful results, indicating the nature of the action between the hide and the tanning material, but only recently has science obtained a hearing in the industry. The reason for this is not far to seek; the changes involved in tanning are exceedingly complex in character, and depend to a large extent upon the properties of substances in a colloidal condition. Examples of this state are to be found in solutions of gelatine and starch having properties different from ordinary solutions, such as that of setting with the formation of a jelly. The scientific study of the colloidal state is now being more vigorously pursued, and as our knowledge of it increases we may expect further advances in the leather industry.

Mineral tannages, of which alum was the first known, are also of interest. The "tawing" solution contains alum and common salt, the latter serving to counteract the swelling of the hide produced by the free acid in the alum solution. Salts of the metals iron and chromium, chemically similar to aluminium, have been used for tanning, and although iron salts have no application as tannages at the present time, chrome tanning is a very important industry, founded and reared upon scientific knowledge. Many patents

have been taken out, including those by Knapp in 1858, by J. W.—later Sir J. W.—Swan, by Heinzerling in 1879 (the first commercially successful process introduced into England) and that by Augustus Schultz, a New York dye works chemist, in 1884. Valuable scientific work has also been done in this branch by Eitner and by Procter. A soft and durable leather can be produced which will fix an acid dye without a mordant.

Leather cloth substitutes for leather, used for covering furniture, for bookbinding, stationery cases, pocket books, and many other useful articles, are also produced under scientific supervision. This industry, however, with that of linoleum and similar material, might have been dealt with as branches of the oil industry had we attempted to deal more comprehensively with that subject.

Apart from skins and hides there are other products of the slaughter-house, such as horn, blood, hair and bristles, waste wool and the like, from which valuable chemicals such as cyanide are produced. Glue, too, is made from the chippings of hides, horns and hoofs, which are washed in lime-water, boiled, skimmed, strained, evaporated, cooled in moulds, cut into convenient pieces and dried on nets. The processes are nowadays supervised by trained chemists.

## CHAPTER VII.

## RUBBER.

RUBBER, formerly commonly called caoutchouc, was originally imported from French Guiana. It was obtained from the *Siphonia elastica*, and from Brazil, from the *Siphonia* or *Hevea Brasilensis*, *lutea* and *brevifolia*, through the port of Para, and later from the *ficus elastica*, or india-rubber tree. It was first brought to Europe in the early part of the eighteenth century, but it was many years before its usefulness was realised. Priestley, the discoverer of oxygen, suggested its use for removing pencil marks and, in 1791, Samuel Piat obtained a patent for making waterproof fabrics by dissolving caoutchouc in spirits of turpentine. Hancock, in 1823, and Macintosh followed on similar lines, but the invention of the vulcanising process by Charles Goodyear, whereby the addition of sulphur gave it the consistency of horn, marked the starting point of still greater developments.

The rubber industry has recognised the importance of scientific control, by botanists and chemists, in planting, cultivation and tapping, with consequent increased yields. Chemists examine the latex, and supervise its drying and preparation for use. The variability of tensile strength is largely dependent on the size of the globules in the latex, which is valued accordingly. No standards of purity have been established, but fine Para is generally considered superior to other varieties.

For nearly sixty years chemists of all countries have devoted much time and labour to its synthetic production in the laboratory. In 1860 Greville Williams isolated a compound, which he called isoprene, from the products of the distillation of



natural rubber. Nineteen years later, Bouchardat showed that a substance very closely resembling rubber could be reproduced from isoprene by the action of strong hydrochloric acid, and that by the action of heat alone isoprene yielded turpentine. The work of the French chemist was confirmed, in 1884, by Professor—now Sir William Tilden, who suggested a formula for isoprene, which subsequently proved to be correct, and also obtained isoprene from turpentine. Later, these researches formed the basis on which the synthetic rubber industry was founded, though German chemists, who have also done good work in this field of investigation, lay claim to having established principles the credit for which was clearly not due to them. Among other British chemists who have contributed to the investigations on the subject may be mentioned Professor W. H. Perkin, Dr. Strange, and Dr. F. E. Matthews. Two chemically different rubbers are produced: isoprene-caoutchouc and butadiene-caoutchouc. The raw materials, isoprene and butadiene, are obtained from a variety of substances, including turpentine, isopentane (from the rhigolene fraction of American petroleum), coal tar (the material from this source being para-cresol, one of the homologues of carboic acid), starch and cellulose. The raw material is converted into caoutchouc by methods, involving (i.) polymerisation, by heating under pressure with a suitable substance such as acetic acid, and (ii.) polymerisation, by the action of sodium. The latter method, discovered almost simultaneously by F. E. Matthews in England and Harries in Germany, is the more convenient and gives the greater yield, although the resulting product does not vulcanise so well as that from the former method. All this is progress. As in the case of indigo, science, if successful, will help one form of industry to the detriment of another; the scientific work on the plantations tends constantly to increased yields and economical working, and the artificial rubber has not as yet displaced the natural either in its properties or in cost of production.

## CHAPTER VIII.

## MORTAR AND CEMENT.

THE simplest and most ancient cementitious material is mud, which is still used, reinforced by sticks and grass, by African natives in the construction of their huts. Ordinary mortar is made of water, lime, and sand intimately mixed together. Science has shown that there is no chemical union between the lime and sand; that the sand acts simply as a diluent, preventing undue shrinkage, which occurs when lime is used alone; that the setting is due to loss of water, and that the hardening is caused by the gradual formation of interlacing crystals of calcium carbonate, which effectively bind the material into a coherent mass.

Long before these facts had been established, experience had proved that a pure or "fat" lime produced a better mortar than an impure lime. In the case of hydraulic mortars and cements, however, the knowledge of their structure and action was indefinite until 1887, when the researches of Le Chatelier were published, though a fairly systematic investigation of the nature of hydraulic mortar or rather of the hydraulic limestones employed in its manufacture, was made about the year 1756 by Smeaton, whilst searching for the most suitable binding material for the foundations of the Eddystone Lighthouse, which he had been commissioned to rebuild. He consulted his friend Cookworthy, a chemist, who instructed him in the analysis of limestones, and he found that clay was an essential constituent of a hydraulic limestone, the poor lime obtained on burning it being far superior to fat lime for making mortar intended to withstand exposure to water.

Cements are made by heating in a furnace an intimate mixture of limestone or chalk and clay to a temperature at which clinking takes place. The product is broken up, finely ground, and put upon the market as cement. "Roman" cement was first made by James Parker in 1796, by heating argillaceous limestone containing, already mixed, the two necessary ingredients. The manufacture of Portland cement was founded on attempts to imitate Roman cement, using a mixture of lime and clay instead of the argillaceous limestone. Nothing was understood of the why and the wherefore of the process, and often the best part of the product was rejected in the unslakeable portions. Chemical action in the furnace was unthought of, and even when it was evident to scientific men and duly published, considerable time elapsed before the manufacturers took advantage of the efforts of science towards the furtherance of their industry. It is now known that chemical action between the lime and the clay in the furnace effects the formation of silicate and aluminate of calcium. When the cement is treated with water, these compounds are decomposed with the production of slaked lime, and the acids derived from silica and alumina. These substances again interact, with the formation of the hydrated silicates and aluminates as interlacing crystals, giving tenacity to the preparation, with the result that first setting and subsequently hardening take place, these phenomena being merely stages in one process. Thus the researches of chemists have established facts which have been most serviceable to the cement maker in increasing the efficiency of his product through the choice and treatment of the best materials.

We owe more than this, however, to the study of the chemistry of cement. It remained for chemists to show the dangerous effect of certain impurities, such as magnesia, in excess, and sulphates, on the resistance of cement to the attack of water. - Such substances must be carefully excluded within well-defined limits. When cement is used to make

concrete foundations exposed to sea water, the mass must be either very compact and impervious, or be covered with an impenetrable stone facing, for the reason that sea water contains sulphates and salts of magnesium in plenty, and, consequently, if penetration by the water takes place, the cement decomposes and the life of the structure is correspondingly shortened.

It is obvious that for such a substance, on which the stability of costly buildings and structures so largely depends, the provision of a definite standard specification became a necessity. The British Standard Specification was formulated in 1904 by a sub-committee, appointed by the Engineering Standards Committee, including engineers and contractors, chemists, architects, manufacturers, and representatives of official bodies using large quantities of Portland cement for public works. The specification provided for both chemical and mechanical tests, and, although subsequently modified in the direction of improving the quality of the cement supplied under the specification, remains essentially the same to-day—a definitely scientific safeguard accepted alike by producers and users.

We have indicated how the explanation of scientific phenomena tends to improvement in manufacture, and it is interesting to note that a reason has been advanced for the use of straw in the making of bricks by the Israelites. It is not a suitable binding material, but Acheson has shown that clay is rendered more plastic by the addition of tannin, and that an extract obtained by soaking straw in water produces the same effect. The Israelites complained, therefore, of the hardship of working with less suitable materials, while they had to produce the same tale of bricks. Possibly the use of grass assists in the same way the African natives in making their mud huts.

## CHAPTER IX.

## REFRACTORY MATERIALS.

A MATERIAL is termed *refractory* when it resists the ordinary treatment to which materials of its class are subjected ; it may be a mineral which does not yield readily to the hammer, or an ore not easily reduced. In recent times, however, the term has become specially associated with substances that will resist economically the temperature of a furnace, and the corrosive action of other substances with which they come into contact. Refractoriness may, therefore, be a vice or a virtue, according to circumstances, and a given material may be refractory in one process, but break down easily if employed in another.

The increased demand for refractory materials during the war, particularly in the manufacture of steel and glass, has shown the need for further scientific investigation. Experiment on the large scale is costly, especially if carried out in an unscientific manner. The help of chemists is therefore essential in determining the composition and the chemical and physical properties of such substances, having in view the purposes to which they are to be applied. The work is not confined to the investigation of known refractories, but is extended to the discovery and utilisation of new refractories to cope with the conditions created by their employment in high temperature furnaces.

Having selected a suitable material, from the chemical point of view, it is necessary to ascertain whether it will withstand, without shrinkage, fusion or softening—and consequent deformation—the temperature required for the desired reaction. The refractory that will last for ever has yet to be found, but that with the longest life is the most economical,

provided the saving effected by the increased length of life—renewals being less frequently required—plus the saving of time and labour, in more continuous running of the furnace, is proportionate to any additional cost. The subject has long been treated more or less scientifically, the older refractories being classified into acid, basic, and neutral materials. As examples of the acid class we have fire-clays, such as ganister, the highly siliceous material used for lining acid Bessemer converters; in the basic class, such substances as lime, magnesia, and calcined dolomite; while among the neutral refractories we may include gas carbon and graphito. These materials have proved eminently suitable for some purposes, but with the use of the electric furnace we require substances still more refractory, and in recent years science has provided a number of them.

Carborundum, the extremely hard and refractory carbide of silicon, was first made in 1891 by Acheson, who obtained it by heating graphite with sand in the electric furnace, and it is now employed as a refractory lining for such furnaces, besides being useful as an abrasive. It has also been incorporated with cement to give grip to surfaces, as on staircases subjected to considerable wear. Other modern refractories are alundum—fused aluminium oxide—silicon, fused silica, zirconia, and artificially made graphite. Crucibles of graphite, intimately mixed with sufficient clay to give the mixture coherence, are far preferable for many purposes, and much more durable than those made of clay alone.

## CHAPTER X.

## GLASS AND ENAMELS.

THE manufacture of glass dates from the first period of Egyptian history. Egypt, the instructor of the world in so many arts, possessed in very early times craftsmen skilled in making, blowing, colouring and cutting this most remarkable and useful material. The industry survived through the vicissitudes of the country until the time of Tiberius (A.D. 14-41), who brought Egyptian glass workers to Rome, where the art flourished until the decline of the empire, during which the principal centre of manufacture was transferred to Byzantium. The value attached to glass by the ancients is indicated by the circumstance that the industry was always supported and encouraged by the most powerful and influential rulers, migrating with their power from one country to another. However, at the time of the fall of Constantinople it had become established in various centres, of which the chief was Venice, where it soon attained such proportions as to give occupation to over 8000 persons.

In the Middle Ages the industry was developed in Germany and Bohemia, especially in the latter country, which, owing to the native supply of pure quartz, ultimately superseded Venice as the source of the finest glass. In 1870 glass making gave employment to 30,000 workers in Bohemia. The invention of glass mirrors has been attributed to the Germans, the original method being to back the glass with polished metal. Glass was first used for windows in England about the end of the eleventh century, and was made here in the fifteenth, but with little success until about 1557, when French artisans were employed in London. In 1670 Venetian workers were brought over to make

the heavier and finer kinds, and in 1771 the industry became more firmly established by the formation of the British Plate Glass Company, whose successors are still in existence at St. Helens.

The scientific study of glass was first made on the physical side, its transparency, permanence, and the absence of crystalline structure with consequent birefringence, combining to render it an almost ideal material for the construction of the essential parts of optical instruments. In fact, the science of optics, with its manifold applications to spectacles, microscopes, telescopes and spectroscopes, owes its existence to our possession of glass. The first investigations in the chemistry of the subject were made with a view to the improvement and better adaptation of glass to optical purposes. Up to 1829 the only varieties of optical glass were soda-lime or crown glass, potash-lime or Bohemian glass, and potash-lead or flint glass, also known as crystal or strass, these being made from mixtures of the silicates of the metals indicated. Before that year Fraunhofer and Guinand had made experiments modifying the composition of crown and flint glasses, and had produced compound lenses with a fair approach to achromatism. In 1829, however, Döbereiner produced glasses containing barium and strontium, metals closely allied to calcium, the metal contained in lime, and in 1834 Harcourt, in England, commenced a long series of researches on the production of new glasses, which—although the positive results obtained were of small value—established principles subsequently turned to good account in the manufacture of special kinds for thermometers, laboratory apparatus, lamp chimneys, optical instruments, and many other important articles. The next advance, an epoch-making one, was begun about 1880, when Schott, a trained chemist, the son of a Westphalian glass maker, was encouraged by Abbé to search for new and better optical glass. His knowledge of mineralogy served him well, for instead of proceeding laboriously along the lines of methodical research, he took almost a direct road to the desired goal, producing glass con-



taining boric and phosphoric oxides with alumina and baryta. Microscopes designed for these new glasses proved perfectly achromatic, and in every way superior to the older kinds; and this striking advance has doubtless contributed enormously to the usefulness of the microscope, and of the microscope to industry generally.

Schott next turned his attention to the solution of the problems of thermal expansion and volume temperature hysteresis of glass. Owing to its low thermal conductivity it is important that glass intended to withstand sudden changes of temperature should have a thermal expansion as slight as possible, in order to hold against the strain set up by unequal temperature changes, and so that the risk of cracking may be minimised within reasonable limits; the range of temperature change varying inversely as the thermal expansion. Pursuing his investigations, Schott produced borosilicate glasses with exceedingly low coefficients of expansion, and capable of resisting a sudden temperature change of over 190 deg. Cent., whereas the ordinary Bohemian glass would scarcely withstand a change of much over 90 deg. The borosilicate glasses have therefore been of service for the construction of incandescence gas chimneys, and also of apparatus for laboratory use; their slight solubility in chemical reagents constituting an additional advantage.

When a thermometer made of ordinary glass is heated to a temperature much above that of the air the glass bulb, on cooling, does not return immediately to its original volume, and may take months or even years to do so. Consequently if the bulb, before it has regained its original volume, is surrounded by melting ice, the thermometer will not register the true melting point, but a point, varying with the thermometer, from 0.5 to 1 deg. Cent. below the correct temperature; and lower temperatures in general will not be registered correctly until the bulb has regained its original volume. This defect was largely overcome by the results obtained by Schott, whose Jena normal glass 16<sup>111</sup> and Jena borosilicate glass 59<sup>111</sup>, when used for

thermometers, show a zero depression of only about 0.05 deg. Cent. after heating to 100 deg. Cent. Owing to their infusibility, glasses of this type can also be used for nitrogen-filled thermometers, registering up to about 575 deg. Cent.

The list of new and useful scientific products might be much further extended if we were to deal with the subject more thoroughly, but it would be regarded as an oversight if we omitted to mention fused silica glass, a comparatively recent invention. From pure quartz worked in the oxy-hydrogen flame excellent glass is produced, having the property of withstanding a sudden change of temperature of over 1000 deg. Cent. Being highly resistant to chemical action, it is useful in the laboratory for many purposes for which platinum was formerly employed.

Until the outbreak of war the production of glassware for use in chemical investigations was almost exclusively in the hands of Germany and Austria. Stocks were becoming speedily exhausted and the position would have become serious for many important industries if British chemists had not promptly taken the matter in hand. They had not merely to imitate glasses previously imported, but to find substitutes for certain ingredients of batch mixtures, notably potash, for which also we had hitherto been dependent on Germany and of which supplies were running low. The work of Professor Herbert Jackson\*, in conjunction with the Glass Research Committee of the Institute of Chemistry, was especially successful, and, with the co-operation of a number of well-known firms, laboratory vessels, such as beakers and flasks, and all ordinary forms of apparatus are now produced in this country, having qualities in some respects superior to those of enemy origin. In some cases, perhaps, the products have not quite the same finish as those of the experienced German workers, but we are convinced that the defects are not radical, and that given time, the British makers will not only equal, but excel the German in both quality and technique.

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\* Now Sir Herbert Jackson, K.B.E.

In addition to the needs of the laboratory, many other kinds of glass were required, and the work was extended to the investigation of over forty varieties for which formulas have been supplied to approved firms. With shortage of labour and other economic difficulties, firms have undertaken with remarkable energy new branches of work which it is hoped they will be able to sustain, in the future, in the face of competition from our quondam enemies.

Yet another problem has been successfully tackled by Professor Jackson for the Ministry of Munitions, viz., the treatment of clay used for making vessels employed in glass production.

For the production of optical glass essential to the services, we, fortunately, had well-established manufacturers, by whose praiseworthy endeavours the output has been sufficient to cope with the greatly increased demand. Professor Jackson has supplied formulas for batch mixtures for several important varieties not hitherto made in this country. The difficulty of securing supplies of suitable sand had also to be faced, and our mineralogists and chemists devoted attention to this question, with satisfactory results, the report of Dr. Boswell, of the Imperial College of Science and Technology, indicates that we possess natural resources which can be utilised by our manufacturers to their advantage. Research work on refractories and electric furnace methods is also in progress at the National Physical Laboratory.

In the course of time an enterprising firm, with the aid of chemists and from indigenous sources, produced supplies of potash of high quality in sufficient bulk for the imperative requirements of glass makers, and this factor was of no small consequence, since it is admitted that for certain glasses potash is practically indispensable.

From the foregoing, it is evident that in spite of the antiquity of the industry, and the fact that good glasses for ordinary and ornamental purposes were produced independently of modern science, many special glasses owe their origin entirely to scientific investigation. It is not too much to say that on the

possession of such glasses in time of war may depend the fate of many a good ship and many a good man. Who can say, then, how great is the debt of the industry to science and of the country to both ?

#### ENAMELS.

The art of enamelling is of remote origin. We have already referred to its application to pottery by the Chinese. It was practised also by the Egyptians and Etruscans, passing in the course of time to the Greeks and Romans ; but we propose to deal more particularly with the enamelling of metals, which appears to have been invented in Western Asia and to have traversed Europe in the early centuries of the Christian era. The history of the subject is of absorbing interest to those who regard it as an art, and much may be gleaned from Bushell's work on "Chinese Art," published by the Board of Education. The Chinese give the credit for its discovery to Constantinople ; the similarity between the methods of the Chinese and the Byzantine enamellers is held to support this opinion. We are concerned here, however, with the utilitarian rather than the artistic applications of enamels. We use them in the manufacture of badges, watch and clock faces, and on surfaces exposed to weather (advertisements), on the blades of exhaust fans, on baths and domestic utensils, and on vessels employed in chemical industry.

An ordinary enamel may be prepared from common glass fused with lead oxide, and rendered opaque by the addition of oxide of tin. Colours may be produced by the addition of other metallic oxides. Thus, from copper we obtain green ; from iron or gold, red, and from cobalt, blue. Small quantities of manganese dioxide give us a fine violet colour and larger quantities black. For the production of good colours, the purity of the raw materials is of the first importance, and the enamel maker looks, therefore, to the help of the chemist to ensure satisfactory results. If an enamel is to be pigmented with copper, the presence of this metal in the raw material will not be objectionable if its degree of oxidation is the same as that of the

pigment used. If the enamel is to be coloured green with cupric oxide and that substance is present in the lead oxide used, the impurity is of small consequence ; but if the enamel is to be coloured yellow with antimony oxide, the green produced by the copper impurity will spoil the effect. The presence of small quantities of ferric oxide in the lime will modify the green produced by copper oxide, and is undesirable unless it be required to tone the green colour, when it can be added to materials originally free from this substance. In any case, the quantity of impurity should be estimated and due allowance made for its effect. Much may depend on the method of preparation of the pigment. For instance, cupric oxide may be prepared by roasting copper filings in air, but the product will not yield nearly such good colours as the oxide chemically prepared from pure copper ; and again, the blue colour produced from commercial cobalt compounds is greatly inferior to that obtained from chemically prepared cobaltous silicate.

Of the methods of preparing chemical and heat resisting enamel for industrial plant little is common knowledge. In some cases the coating consists of two layers, the first being devised to bind with the metal and act as intermediary between the metal and the finishing enamel. Having in view the uses to which such vessels are put, there is plenty of room for further investigation, particularly on the coefficients of expansion of various metals and alloys and the relation of such physical considerations to the composition of the enamels employed. The surface remains good until a craze appears, but once liquid gets to the metal the vessel begins to lose its coating. It is reassuring to know that chemical firms of long standing find British enamel ware, such as evaporating pans, at least as satisfactory as that from Germany, though our manufacturers, as is often the case with other commodities, have been less inclined to put themselves about to supply special requirements, for instance, with regard to the shapes and sizes of the vessels required.

## CHAPTER XI.

## POTTERY AND PORCELAIN.

THE manufacture of pottery is yet another industry which has been handed down from very early times. Pliny attributed the craft, in which the Greeks and Etruscans excelled, to Coræbus, an Athenian, but obviously it was of far greater antiquity, the potter being frequently referred to in ancient Egyptian records to symbolise the Creator of man. The earthenware of the Greeks and Romans was unglazed and porous, but they rendered their vessels impervious by covering them with wax, tallow and bitumen. The invention of porcelain is generally credited to the Chinese. It is mentioned in books of the Han dynasty, the earliest date suggested being about 185 B.C. Its origin has been attributed to attempts made to imitate glass imported from Syria and Egypt. and by some it is supposed to have been discovered accidentally by alchemists in their search for the philosopher's stone. The industry was started in Japan before 27 B.C., and found its way from the Far East to Persia, where it is known as *chini*, coming to us, in the course of time, through Arabia, Spain, Italy and Holland, the potteries of Lambeth being founded by men from Holland about 1640. Porcelain was made in France, at St. Cloud, towards the end of the seventeenth century, and in nearly all European countries in the eighteenth century.

We can only marvel that such porcelain as, say, that of the Ming Dynasty (1368-1643), with all the technique involved in the selection of materials and its treatment, the craftsmanship, colouring and glazing, was produced before science, as we now use the term, had any voice in such matters. The

Chinese hard paste porcelain consisted of kaolin in a pure and very finely divided state, and petuntze (finely ground felspathic stone); and the glaze was made from selected petuntze mixed with specially prepared lime.

One of the first European makers of fine porcelain of whom we have records was Böttcher, a Saxon chemist who was placed in charge of the Meissen factory, established in 1710, the methods employed being kept secret. Pott, a Prussian chemist, endeavoured to compete with him, and although his efforts were not successful, his researches on materials likely to be useful in porcelain manufacture gained for the industry some helpful knowledge. About the middle of the eighteenth century 700 men were employed at Meissen, but in the meantime Stölzel, who escaped from the factory about 1720, founded the Austrian industry at Vienna, where 500 men were employed in 1785. Mention should also be made of the circumstance that William Cookworthy, chemist of Plymouth, to whom we have already referred in connection with cement, found kaolin at Tregonning, near Helston, and took out a patent in 1768, which he worked at Plymouth for two or three years before establishing a factory at Bristol. We must admit that the claims of science so far were slender, and we do not propose to pursue the history of the subject further; but science required for her own purposes porcelain resistant to chemical action, heat, and variations of temperature. The production of Royal Berlin basins and crucibles for the laboratory could only be secured by careful selection and utilisation of the most suitable materials and much painstaking experiment. Science examined the processes employed and explained the changes involved, while one notable achievement, viz., the discovery of means for measuring high temperatures, found direct application in the industry. The temperature of kilns is a factor of no little importance, and is usually determined by cones made of oxides of iron, aluminium, and silicon. The softening points of the cones are known with reasonable accuracy—a

series of thirty-six allowing for the observation of sufficient range of temperature in porcelain burning. As the temperatures exceed 1000 deg. Cent. ordinary thermometric methods are not applicable. The series of cones could only be constructed and standardised with the aid of physical science, which has provided Le Chatelier's thermo-electric pyrometer, Callendar's platinum resistance thermometer and the Féry radiation pyrometer. Their use in the standardisation of the cones, however, is, of course, insignificant compared with their use in metallurgical operations.

For supplies of porcelain for laboratory purposes this country has hitherto been mainly dependent, as in the case of glass, on Germany. Our chemists have taken the matter in hand, however, and remarkable progress has been made by several British manufacturers. Research on the subject of hard porcelain is progressing, and there is good ground for hoping that this branch of the industry will be retained here in the future.

The danger to workers of lead oxide as a constituent of glazes for earthenware has also provided a problem for chemists. The employment of lead silicates instead of oxide, as suggested by Thorpe and Simmonds, is less harmful; and the lead glazes have been largely superseded in recent years by mixtures containing silica, alumina, potash, and soda, with about 10 per cent. of boric acid to increase the fusibility. Where lead is an essential constituent it is applied in the form of silicate.



## CHAPTER XII.

## CHEMICAL PRODUCTS.

IN our second chapter we have dealt with the heavy chemicals and alkalies, and we will proceed now to consider the production of other chemical substances of value in industry, or useful for domestic, medicinal, scientific, or other purposes. The importance of this branch is so wide and fundamental that it is not too much to say that industry as a whole is largely dependent on an adequate supply of chemical products. The field is so great that we cannot attempt to indicate all or nearly all the substances coming under this head, but we will choose a few examples of different types, all rendered available by scientific methods.

*Acids.*—Certain acids, such as tartaric, citric, lactic, oxalic, formic, salicylic, benzoic, acetic, hydrofluoric, boric, and arsenic acids are not prepared on a scale comparable with that of sulphuric, hydrochloric, and nitric, but their value in technical operations and for other purposes warrants their industrial production in a condition more or less pure, according to circumstances. Tartaric and citric acids, from vegetable sources, and lactic acid of animal origin, are used in calico printing. The first is an ingredient of baking powders and effervescing medicines, such as seidlitz powders, and the second is used in the production of summer beverages. Oxalic acid, which is prepared by heating sawdust with a mixture of caustic potash and soda in the presence of air, is also used in calico printing, and its acid salts are valuable as detergents, under the name of salts of sorrel or salts of lemon. Formic acid is useful in dyeing and tanning, and it is interesting to note that it was formerly obtained by distilling

red ants, but is now made by heating caustic soda with carbon monoxide under pressure. Salicylic acid, which is prepared from phenol, is used in the production of various drugs, of which aspirin is an example, and is employed as an antiseptic. Benzoic acid, from toluene, finds application in the manufacture of dyes and as a preservative; acetic acid in bleaching, dyeing, and calico printing, and in the manufacture of artificial vinegar. Hydrofluoric acid, which is obtained by the action of sulphuric acid on fluorspar, comes on the market as an aqueous solution in gutta-percha bottles, and is used for etching glass as well as for antiseptic purposes. Boric acid, from mineral sources, is valuable as a constituent of various kinds of glass, and is used as an antiseptic and a food preservative. Arsenic acid is employed in dyeing and in the preparation of certain aniline colours.

*Bases.*—Among the common bases we have caustic potash, caustic soda—with which we have already dealt—strontium hydroxide, and magnesia,—alkaline metallic oxides capable of neutralising acids with the production, by double decomposition, of salts and water, the metals replacing the hydrogen in the acids. Caustic potash is prepared either by electrolysis of the chloride or by the action of lime on a solution of potassium carbonate, that salt being obtained from the chloride by a modification of the Leblanc process or by a method identical in principle with the ammonia-soda process, in which trimethylamine—of which something will be said later—takes the place of ammonia. For some purposes the cheaper base, caustic soda, is equal in efficiency to the more expensive but more powerful potash; but for others the latter is more economical—for instance, in the production of oxalic acid from sawdust on the large scale. When caustic soda alone is used, the yield of acid is not more than a third of that obtained by the use of caustic potash or of a mixture of potash and soda. On the other hand, in the analysis of flue gases, a valuable check on fuel economy, a soda solution of pyrogallol acid is

a very much more rapid and efficient absorbing reagent for oxygen than a potash solution of the same. Caustic potash decomposes most metallic salts, and at a high temperature acts with energy on many substances. It is employed in numerous industrial operations, and is ordinarily used for the manufacture of soft soap, in which it is combined with the fatty acids derived from the drying oils, such as linseed, whale, and seal oils.

Strontium hydroxide, prepared mainly from the mineral sulphate, is largely used in the extraction of the uncrystallisable sugar from molasses. The native carbonate requires a higher temperature for calcination to oxide than does calcium carbonate to lime. However, in certain sugar works, where fuel, including exhausted cane, is cheap, this process is used for the production of the material.

The use of magnesia in the ammonia-soda process, and also as a refractory material, has already been mentioned. Considerable quantities are consumed in medicine as an anti-acid.

*Salts.*—The salts of technical importance are very numerous. Those of sodium, on account of their cheapness, easy solubility in water, and comparative harmlessness, are in constant use in many industries, and are often interchangeable with potassium salts; but in some cases the special properties of the latter yield better products for manufacturing purposes. Potassium permanganate and chlorate can be crystallised better than the corresponding sodium salts, and are therefore obtainable in a higher state of purity. Potassium nitrate is used in the manufacture of ordinary gunpowder, whereas the use of sodium nitrate would be impracticable on account of its ready absorption of atmospheric moisture. Potassium sulphate, a constituent of ordinary alum, occurs as the mineral kainite, and is valuable as a fertiliser. Potassium ferrocyanide and bichromate are ingredients in the production of certain pigments, and the latter finds employment in tanning and photography, as well as in the cells of bichromate electric batteries.

Both these salts are now largely replaced by the cheaper sodium compounds, owing to the stoppage of supplies from Germany. A mixture of sodium and potassium cyanides obtained by heating potassium ferrocyanide with metallic sodium is used in the MacArthur-Forrest gold extraction process. Sodium nitrite and hypochlorite are largely used in the production of dyestuffs, and, indeed, the fact that the former was hitherto obtained almost exclusively from Germany formed no small obstacle to the manufacture of certain important dyes in this country. Sodium thiosulphate—hypo—is used in bleaching as an antichlor and in photography as a solvent for silver halides. Sodium silicate—water glass—is used for preserving eggs and also for protecting carbonate stone buildings from the action of weathering.

Ammonium sulphate we have already mentioned as an artificial manure. The chloride is used in soldering, and its solution forms the electrolyte in Leclanché cells. The nitrate is the source of "laughing gas," and the commercial carbonate is commonly the principal constituent of "smelling salts."

Mention must also be made of certain peroxy compounds, some of which have attained considerable technical importance in comparatively recent times. Sodium peroxide is obtained by the action of hot air on sodium contained in aluminium trays. The percarbonates and persulphates of sodium, potassium, and ammonium are prepared by methods of electrolysis. Barium peroxide is made by heating the oxide to a dull redness in dry air, free from carbon-dioxide, and is used in the manufacture of hydrogen peroxide, which, as are other peroxy compounds, is largely applied as a bleaching agent for cellulose materials.

The salts of barium and strontium are very useful in pyrotechny, the former for producing green and the latter red light. Magnesium sulphate is Epsom salts. Mercury salts, including calomel, are also employed in medicine. Mercuric chloride or corrosive sublimate is an excellent antiseptic, and the fulminate is a useful explosive. Zinc chloride is used for the

destruction of insects and parasites, and other zinc compounds are of medicinal value. Gold, silver, and platinum salts are extensively used in photography, and copper, tin, and antimony salts in dyeing and calico printing. Copper salts are also important in the Deacon chlorine process, in electrotyping, in the manufacture of pigments, and the protection of wheat from smut. Lead carbonate, or white lead, is used in large quantities in paint manufacture, and the azide is an explosive body, which may be employed in percussion caps. Bismuth and iron salts find good use in medicine, the sulphate of iron being also useful in gold extraction.

*Solvents.*—Water, the commonest and most useful solvent, cannot be discussed here for the obvious reason that under ordinary conditions it is not a chemical product from our point of view. Water purified by distillation, however, is a commercial article, and might perhaps be included. Among inorganic solvents, mention must be made of ammoniacal copper solution for cellulose, and sulphur chloride, which is prepared by the direct union of the elements and is a valuable solvent for sulphur, being largely employed in vulcanising rubber. The common acids, such as nitric, sulphuric, and hydrochloric, are excellent solvents for metals and oxides, but the solutions so obtained are not simple, the original metal or oxide not being recoverable by merely evaporating the solvent. Alcohol, or spirits of wine, prepared by the rectification of fermented liquor, is a valuable solvent in many ways, such as, for instance, the purification of certain organic products by crystallisation from alcoholic solution.

In manufacturing processes, substances, such as fatty oils, rubber, and sulphur, which are insoluble in water, are frequently required in the form of a solution, and it rests with the chemist to discover the best solvents for such substances and the methods of preparing and applying them. Carbon disulphide, a volatile, poisonous, highly refracting liquid, heavier than water, was discovered in 1796 by Lampadius, who obtained it by distilling

iron pyrites with carbon. As ordinarily met with it has a most obnoxious smell, but when pure the odour is ethereal and not unpleasant. It occurs in the products of the destructive distillation of coal, but is manufactured mainly by the direct union of charcoal or coke with sulphur in retorts or in the electric furnace. Its uses are many; it dissolves sulphur, gums, rubber, phosphorus, resins, essential oils, iodine, and alkaloids. It is used sometimes for the extraction of fatty oils remaining in the residue after crushing seeds, being subsequently removed by distillation and used again. A solution of sulphur in carbon disulphide is used for the vulcanisation of rubber. Its poisonous action has been utilised for destroying blight in grain without ill effects—except to the blight; and potassium thiocarbonate—a compound of carbon bisulphide and potassium sulphide—is destructive to insects which infest vines. On account of its high index of refraction, hollow glass prisms filled with carbon disulphide are employed in spectroscopy. A solution of iodine in carbon disulphide is of use in certain physical experiments, for the reason that such a solution is opaque to rays of light, while it transmits heat rays freely. Lastly, we may mention that from carbon disulphide and chlorine is obtained carbon tetrachloride, a solvent for fats, which is also employed in the production of certain dyes, and being non-inflammable, serves a useful purpose in fire-extinguishing apparatus.

Among the organic solvents are several that are also anæsthetics. Chloroform was discovered simultaneously by Guthrie, an American, and Souberain, a Frenchman, in 1831, and was first employed as an anæsthetic by Lawrence in London, and Simpson in Edinburgh, in 1847. It is prepared on the large scale by the action of chloride of lime on alcohol or acetone, the product being a valuable solvent for fatty oils, india-rubber, alkaloids, resins, and other substances. Prepared by the above process, however, it contains highly poisonous impurities, which are gravely detrimental to its use as an anæsthetic, for which

purpose it is obtained by distilling chloral—resulting from the action of chlorine on alcohol—or its hydrate with caustic soda, the final product being sufficiently pure.

Ether, another solvent, also an anæsthetic, was known in the sixteenth century, and described by Valerius Cordus, a German physician. It was prepared by the action of sulphuric acid on alcohol, and in the early part of the eighteenth century was employed as a mixture with alcohol, under the name of Hoffmann's Anodyne, to allay pain. Its use as an anæsthetic was discovered by Charles Jackson, of Boston, in 1842. The most economical method of manufacture is the continuous process, devised by Boullay.

Acetone, a valuable solvent for oils, and employed largely in the manufacture of explosives, is found in the free state in the products of the destructive distillation of wood, and is obtained by the dry distillation of acetate of lime, which substance is also produced from pyroligneous acid.

*Fine Chemicals.*—The many substances we have mentioned under the heading of chemical products, represent only a very small proportion of those in common use, and do not include all that are employed in the laboratory, or those at present of purely scientific interest, which are very numerous. We say "at present" purposely, for no one can tell how soon they may find practical application. The value of "research for its own sake" has already been shown in the many examples we have cited of the discovery of elements and compounds, at first merely regarded as scientific curiosities, but sooner or later proved to be of incalculable importance to industry and to the world. So much depends on the accuracy of analytical results, that an adequate supply of chemicals in a sufficiently pure state to be used as reagents is an essential requirement in all laboratories. The statement should be too obvious to mention, but it must be remembered that we buy and sell on analytical data; we check and control vast technical operations on such data, and must be able to rely on

sound reagents in most chemical investigations. German fine chemicals have enjoyed a reputation for purity, but of chemicals generally, apart from dye-stuffs, we produce the bulk of our own requirements; our export trade has been greater than that of our continental competitors, and there is no doubt that, with increased scientific control and care, we can manufacture products of equally high standard.

A number of concerns of established repute are now energetically developing the fine chemical industry. The processes of manufacture and purification call for the services of highly trained chemists, of whom the supply will certainly be forthcoming as the demand for them increases.

A pamphlet prepared by a special committee appointed by the Councils of the Institute of Chemistry and of the Society of Public Analysts, was issued early in 1915, giving details of the tests for purity of a number of important analytical reagents. This provides a standard for the manufacturers who will still continue to make products of other grades for various uses, while producing the fine chemicals up to the specification standard at a higher cost, which the consumer is always willing to pay. For one example out of many, sulphuric acid for many technical purposes is highly impure. In some cases the impurities are substances which do not affect the behaviour of the acid and its suitability for the purposes for which it is required. A purer acid is made for general laboratory use; but for good analytical work the acid must be free from lead, calcium and other metals, from arsenic, selenium, nitrogen and halogen compounds, and from reducing substances, and should leave no solid residue on evaporation to dryness. Tests are prescribed whereby such impurities may be detected, but it is most advantageous to be able to secure reliable supplies without the necessity of applying them, and possibly being obliged to purify the substances in the laboratory before using them. The purification of sulphuric acid on the small scale is an expensive, difficult, and tedious operation. It is a hopeful sign therefore that a number of our well-



known manufacturers are now producing guaranteed analytical reagents of recognised standard degrees of purity.

*Drugs.*—After all the references we have made to the work of the chemist in industry, we do not need to labour the distinction between the man who practises chemistry and the man who practises pharmacy. The latter has to depend on the former for many of the materials he employs in dispensing, or the physician may prescribe with very uncertain results, and the patient perish, or, in any case, pay to no purpose. The subject of drugs and pharmaceuticals, with all its ramifications into the substances compounded into medicines of all kinds, pills, powders, ointments, lotions, tinctures, and so forth, is too extensive for us to treat adequately, and we can only deal with the subject by indicating a few developments in this important branch of industry.

Many of the drugs used in medicine are of vegetable origin. Quinine, for instance—discovered in 1820 by Pelletier and Caventou—is extracted from the bark of trees of the *Cinchona* species. Strychnine is obtained from the seeds of various plants such as *Strychnos nux vomica*. Atropine is prepared from deadly nightshade juice, which contains two alkaloids, hyoscyamine and hyoscyne. The juice is treated with caustic potash, the hyoscyamine being thereby converted into atropine. The mixture is shaken with chloroform and the solvent evaporated, the atropine being extracted with dilute sulphuric acid, precipitated by potassium carbonate, and re-crystallised from alcohol. A solution of the alkaloid has the property, when placed in the eye, of dilating the pupil, a most useful aid to the ophthalmic surgeon.

An increasing number of useful organic drugs, including alkaloids, is now made synthetically from other chemical substances. Many of these are unknown in Nature, their production and utilisation being solely due to science. Salicylic acid and its derivatives, including aspirin, are made from phenol, and used extensively in the treatment of rheumatic and nervous disorders. On account of certain objec-

tionable physiological properties, attempts have been, and are being, made to obtain other derivatives that have no such disadvantages, and good results have been obtained with acetylsalicylic anhydride and cinnamoylsalicylic anhydride. The antipyretics, phenacetin and antifebrin, are made from phenol; antipyrène, which is put to similar uses, being the product obtained by methylating the pyrazolon derivative formed by the condensation of acetoacetic ester with phenylhydrazine. Derivatives of antipyrène include salipyrène and tolypyrène. Veronal is another synthetic drug.

The use of metallic compounds, as bactericidal agents, has long been known. Compounds of mercury have long been used in the treatment of certain diseases. Recently the researches of Ehrlich on the organic compounds of arsenic have done much to alleviate suffering, such complex bodies being much less poisonous to human beings than are the simpler compounds of arsenic. Salvarsan and neosalvarsan have met with success. One of the simplest of such derivatives, atoxyl, has been used in the treatment of sleeping sickness.

Local anaesthetics, administered hypodermically, include cocaine, novacaine, and stovaine, the first being extracted from the coca plant by alcohol acidified with a small quantity of sulphuric acid, and the two latter being synthetic products.

Among antiseptics we must again mention phenol (now being manufactured from benzene in large quantities for making explosives), cresols, formaldehyde, mercuric chloride—corrosive sublimate—and boric acid; while as disinfectants and insecticides, bleaching powder, carbolic acid, potassium permanganate, naphthalene, and zinc chloride—all chemical products—are now largely used.

## CHAPTER XIII.

## PHOTOGRAPHY.

THIS beautiful and now almost essential art is dependent upon the action of light on various chemical compounds, principally the salts of silver. It was first observed by Boyle about the middle of the seventeenth century, that *luna cornea*—silver chloride—darkens on exposure to light, and this phenomenon was further investigated by the Swedish chemist, Scheele, in 1784. No attempt, however, was made to utilise this property for the production of pictures until 1802, when Thomas Wedgwood obtained prints of leaves and other flat bodies on sensitive surfaces prepared by moistening white leather or paper with silver nitrate solution. Similar experiments were carried out by Sir Humphry Davy, but the pictures produced lacked one important advantage; they were not permanent in daylight, and therefore had to be kept in the dark and examined only in weak, artificial light. The next workers of note were Niépce and Daguerre, a great advance being made by the latter, when, in 1839, he introduced a new departure, well-known as the daguerrotype process. This was long ago superseded by other and better methods, but it served the purpose of indicating the right road to success. A plate of polished silver was exposed to the action of iodine vapour, being thereby covered with a film of silver iodide. On exposure in a camera no apparent change took place until development, as is the case with modern photographic plates. The method of development of the Daguerre plates was an accidental discovery. Daguerre, while experimenting, was called away just after he had removed a plate from his camera. For safety, he put the plate in the first dark place that

caught his eye—a box containing odd pieces of apparatus—and when he returned to continue the work, he was surprised to find that during his absence the image on the plate had developed. Investigation of the contents of the box led to the final conclusion that the agent was some metallic mercury loose in the bottom of the box. This provided the means of development, the plates after exposure to light being acted upon by the vapour of mercury. The image was made permanent by dissolving the unaltered silver iodide in the parts less affected by light with a hot solution of common salt, an improvement being almost immediately effected by the suggestion of Herschel, that sodium thiosulphate—“hypo”—was a more suitable fixing agent.

Meanwhile, other investigators had not been idle. In the Calotype or Talbotype process, elaborated by Fox Talbot, and introduced in 1841, we find the principle of modern photography showing signs of active germination. The method depended entirely on the use of papers sensitised with chloride and iodide of silver. In his earlier researches, a piece of paper was covered with silver chloride by immersion, successively in solutions of common salt and silver nitrate. Prolonged exposure in the camera resulted in the production of a negative image, which could be fixed by common salt solution. This method was soon afterwards greatly modified in the following way. The image formed by the camera lens was received on a sheet of paper covered with silver iodide, and was subsequently developed by a mixture of silver nitrate, acetic acid, and gallic acid. When the resulting negative was made transparent by means of wax, positive prints could be obtained by allowing sunlight to pass through the negative on to a piece of the sensitive silver chloride paper. The first use of glass plates was made by Archer in 1851, the glass being covered with a film of collodion in which cadmium or zinc bromide or iodide had been dissolved. The plate was sensitised by dipping into a solution of silver nitrate and it was exposed in the wet state in the camera, the image being developed by washing with

some reducing agent, such as ferrous sulphate. The image being fixed by a solution of sodium thiosulphate or potassium cyanide provided, when dried, a negative from which any number of positive prints could be taken. By this means the detail of the pictures was better than that given by the older processes, and other advantages were obtained, including the shortened time of exposure of the more sensitive collodion film. By this time very many workers had entered the field, and the art made rapid strides. A further improvement was the introduction of dry plates, the sensitive surface being composed of gelatine impregnated with silver bromide; but to give a detailed history of the development of modern photography would be beyond the scope of this article.

The modern dry plates consist of sheets of glass cut to standard size and covered with a gelatine emulsion of silver bromide. The emulsion is prepared by the inter-action of ammoniacal silver nitrate with excess of potassium bromide containing a little iodide in hot gelatine solution, the emulsion formed being kept at a temperature of 45 deg. Cent. for some time—an operation which increases the sensitiveness. The emulsion is then washed free from soluble salts, run in an even coating on to the plates, and dried. After exposure, the plates are developed by the reducing action of certain compounds, such as pyrogallie acid, hydroquinone, metol, ferrous oxalate, and others, with various substances added to modify favourably the course of development. The developed plates are fixed by means of a solution of sodium thiosulphate, well washed and dried. The introduction of celluloid films has lessened the inconvenience attached to the bulkiness and rigidity of plates, films being invariably used when compactness and lightness of outfit are required.

Many kinds of printing paper are available at the present time. Silver chloride papers, both in gelatine and collodion, are used for daylight printing, ordinary P.O.P. being toned with a solution containing gold chloride before fixing with hypo. Self-toning papers require washing and fixing only,

the paper already containing the necessary gold, but modifications of tone may be obtained by washing the prints in a solution of common salt before fixing. Silver bromide and silver iodide are the sensitive bodies in bromide and gaslight papers, of which many varieties are on the market, these papers requiring development, as in the case of plates. Beautiful tones may be obtained by platinotype papers.

Other methods of printing include the carbon process, depending upon the fact that when a gelatine solution of potassium bichromate is exposed to light, the gelatine becomes insoluble in water. Brilliant black and white prints may be obtained by the adhesion, after washing, of finely divided carbon to the insoluble gelatine surface. The paper for the blue prints familiar to engineers is prepared by immersion in a solution containing potassium ferrocyanide and ferrous ammonium citrate, the prints merely requiring to be washed in water and dried. Other methods have been devised to obtain engineers' prints in various colours on a white ground, but for most purposes the blue print method is adequate.

Colour photography, which has attracted much attention during the last few years, has been developed with some success. Many processes have been devised, one of the most striking being the mirror method of Lippmann, which depends upon the interference of direct and reflected rays at different depths in the film, the ultimate deposition of metallic silver produced by development occurring at a distance from the reflecting surface fixed by the wave length of the impinging light. On viewing the developed and fixed plate similar interference phenomena take place with the consequent natural colouring of the image. With the aid of orthochromatic and of panchromatic plates, prepared by the use of various dyes, combined with screens or colour filters, excellent coloured photographs may be obtained. Three-plate and single-plate processes are available, the latter type being more convenient. The Lumière process is a single-plate process, in which the screen consists of a mixture of starch grains, dyed red,

green, and blue, incorporated in a single layer in the plate. All these colour photography processes, however, are still somewhat expensive.

Mention could be made of many debts to photography, including the discovery of radioactivity, which was directly due to the sensitiveness of the photographic plate, the discovery of stars too faint to be observed by the most powerful telescopes, the invention of photo-mechanical processes employed in illustrating books and journals, photomicrography and its numerous applications, and the cinematograph, apart from its everyday uses in peace and war.

*Photographic Materials.*—The manufacture of photographic materials is essentially a branch of the fine chemical industry, since the production of good results depends as much on the purity of the materials employed as on the manner of employing them. Developers, such as pyrogallie acid, metol, and hydroquinone, toning solutions containing gold chloride, and the materials for making and sensitising plates, films, and printing papers must necessarily be pure. In fact, the whole art of photography depends, from start to finish, on a high order of scientific work, both chemical and physical.

## CHAPTER XIV.

## AGRICULTURE AND FOOD.

## AGRICULTURE.

AGRICULTURE, though primarily concerned with the cultivation of the soil—tillage, pasturage, and gardening—may be regarded as the industry to which we look, not only for food—animal and vegetable—but, directly or indirectly, for clothing and textiles, timber, drugs, leather, rubber, and a host of other necessities and comforts. Little reflection is required to show that agriculture is dependent on science, and, although many practical farmers still scout such ideas, the various branches of the industry owe much to geology, biology—botany and zoology—chemistry, physics and meteorology, as well as to the art of engineering. We propose to refer, briefly, to the work of the chemist, especially in connection with the subject of fertilisers.

The fear has been expressed from time to time that, even making allowance for the effects of war, the production of food will fall behind the needs of the increasing population of the earth, unless science can devise measures for coping with the problem. We have shown how, through science, fields devoted to the cultivation of indigo and madder have made way for cereals, and we may confidently expect further changes of the same kind, or even find, in the laboratory, means for obtaining food independently of the processes of Nature by reproducing something akin to the vital processes of vegetable and animal life.

*Fertilisers.*—Mother Earth readily repays the kindly attentions of man and offers an illimitable field to science in the development of food supplies for man and beast. The chemist examines the soil, decides the means to be adopted for the restoration of its



fertility, and barren land is thereby reclaimed. Natural manures, through the agency of which the soil regains its creative energy, are supplemented by artificial fertilisers, and the yield of foodstuffs is increased. Thus, sodium nitrate, found in enormous deposits in certain parts of Western South America, is very largely used as a nitrogenous manure, the crude material being purified by crystallisation. Potassium sulphate, in the form of the mineral kierserite, enriches the soil deficient in potash. Ammonium sulphate, from the distillation of coal and shale, is another valuable nitrogenous manure, and superphosphate of lime, prepared by the action of sulphuric acid on mineral phosphates, provides a fertiliser containing a large proportion of soluble phosphate. The manufacture of this substance, moreover, has been largely instrumental in keeping alive the lead chamber process—chamber acid, as such, being suitable for the purpose.

The calculation of Vergara that the South American sodium nitrate beds would be exhausted by the year 1923 has been proved to be erroneous. Surveys of the known beds show that the supply from them will be sufficient to meet the increasing demand for the next fifty years or more, while the general character of the country leads to the reasonable supposition that other beds of vast extent exist and will be capable of supplying the needs of the world for a further 200 years. However, the end must come sooner or later, and in view of the importance of this substance, both as a fertiliser and as a starting material in the manufacture of potassium nitrate, nitric acid, and other nitrogen compounds, the prospective shortage has given an impetus to research with the object of utilising the nitrogen in the air. One of the methods employed aims at the preparation of nitrates by heating air in a specially constructed electric furnace in which, by a suitable arrangement of electro-magnets, the arc is caused to assume a discous shape. The oxide of nitrogen produced is led away to an oxidising chamber, where it is converted by atmospheric oxygen into a higher oxide, which is

absorbed by bases such as lime, soda, potash, or ammonia. The process, primarily discovered by Sir William Crookes, was adapted by McDougall and Howles, in America, and later by Birkeland and Eyde, in Norway, where electric power is cheap, and bases, manufactured in Germany, were sent to Norway and returned as nitrates.

The cyanamido process, which forms a great German industry, consists in heating calcium carbide with nitrogen in the electric furnace. The nitrogen is obtained from liquid air by boiling off the oxygen, or as residue from water gas or producer gas, which has been used in the manufacture of hydrogen. The cyanamide is applied directly as a manure, and on exposure to water at ordinary temperature slowly evolves ammonia, which, under the action of nitrifying bacteria, is converted into compounds of nitrogen readily absorbed by the plant. It may be noted also that ammonia is easily formed by heating calcium cyanamide with water under pressure. If barium carbide is used instead of the calcium compound, the main yield is barium cyanide, a convenient starting material for the manufacture of other cyanides.

Nitrides, such as those of magnesium, boron, and silicon, are prepared in the electric furnace, and find application as manures rich in nitrogen and as sources of ammonia, though their cost of production is rather high. Many other processes have been patented and used for the fixation of nitrogen, and British chemists have not been idle, in spite of the difficulty of competing against the lower cost of power in other countries. Water power, abundant in Norway, is readily converted into electricity, and is, therefore, a most valuable possession in this connection; but we are assured that an earnest endeavour is being made to produce nitrates in this country at the present time. Incidentally, we would remark that the fixation of nitrogen is of such importance that it is practically certain that if Germany had not solved the problem before the war, she could not have maintained for so long the supply of munitions to her army.

Basic slag—the phosphatic slag from the Thomas and Gilchrist basic Bessemer process—when finely ground is a useful manure for certain purposes, grass land especially deriving benefit from its application. Its employment in other directions has not, so far, been extensive, possibly owing to the existence of a somewhat arbitrary standard of valuation. It is desirable that careful experiment should be made with various crops to ascertain if this standard is reasonable for all purposes. In the result it is not unlikely that great dumps of slag, hitherto regarded as waste, both from the basic Bessemer and from the open-hearth processes, may be available for agricultural purposes.

The quality of artificial fertilisers is to some extent safeguarded by the provisions of the Fertilisers and Feeding Stuffs Act, under which the seller of any artificially prepared or imported fertiliser, and any artificially prepared feeding stuff, is required to give a warranty to the purchaser as to the constituents of value in these articles, and an undertaking that the percentages found in these articles do not differ from those stated in the invoice, beyond certain prescribed limits of error. Official agricultural analysts and samplers are appointed to assist in the administration of the Act, and the Board of Agriculture is empowered to make regulations for the purpose of carrying the Act into execution. It is generally agreed, however, that, with few exceptions, the county and borough authorities concerned have practically ignored it, and beyond appointing officials as required by the Act have given them little or nothing to do, so that offending traders are rarely brought to justice.

*Feeding Stuffs.*—Among the principal artificially prepared feeding stuffs for cattle and sheep may be mentioned cotton cake and meal, which are very rich in albuminoids, as are also cake and meal from the ground nut and Chinese soya bean, and linseed and rape cake, prepared from the marc or refuse from crushing for oil. Other industries provide food material, such as brewers' grains, malt dust and yeast, and beet sugar fibrous wastes.

## FOOD.

While, as we have indicated above, the measures taken to assure the quality of food for cattle are, to a large extent, ineffective, those taken in respect of our own food are certainly more satisfactory, although the Sale of Food and Drugs Acts might, with advantage, be more thoroughly administered in some parts of the country. The term "food" includes every article used for food or drink by man, other than drugs or water, and any article which ordinarily enters into, or is used in, the composition or preparation of human food, and also flavouring matters and condiments; the term "drug" includes medicines for internal or external use. Public analysts are appointed to examine samples—chiefly milk and dairy products—taken under the Act, and proceedings frequently follow both in the interests of health and of the prevention of fraud. Some may protest that the work of the public analyst is not in the interests of industry, but it must be admitted that the honest vendor is directly protected by the prosecution of the fraudulent, and it should be noted also that many prepared foods, such as biscuits, cocoa, margarine, preserved meat, fish, fruits and vegetables, jams and confectionery, and beverages are produced under scientific supervision.

The methods of preservation of perishable food products are due to the application of science. The sterilisation by boiling of meat and of fish, followed by immediate hermetic sealing in cans, is the result of a knowledge of the nature of bacterial life, as also is the practice of preserving by the application of cold, the meat or fish being either actually frozen, or maintained at a temperature near the freezing point without actual congelation. We will refer again to the subject of cold storage later.

The law governing the sale of milk in this country enacts that the content of fat (cream) shall be not less than 3 per cent. The various preservatives available for use are either prohibited, or are restricted as to the quantity that

may be added. This is a necessary precaution, as most of the preservatives, such as formalin and boric acid, are not desirable from the point of view of health, especially in the case of milk, which is so important to infants and invalids. The sterilisation of milk by pasteurisation, which consists in prolonged heating at a moderate temperature, is a useful means of safeguarding the public health, the taste, and therefore the palatability, of the milk being very little affected by the treatment.

Science provides the means of distinguishing between genuine butter and the various substitutes now in common use, such distinction being necessary for the detection of fraud.

Careful investigation by botanical workers, combined with the proper application of manures, has greatly increased the yield of cereals, and the cultivation of many other foodstuffs, such as roots, fruits, tea and coffee, comes more and more under scientific control, with beneficial results. We propose now to consider, as an example, an important foodstuff, in the production of which chemical, botanical and mechanical sciences have played no mean part.

#### SUGAR.

Sugar is contained in the sap of many trees, such as the date, palm, and the maple, and in nearly all fruits. The main sources, however, are the sugar-cane and the beet. The extraction of sugar from cane is said to have been practised in Bengal and in China about 800 B.C., and existing records indicate that the Egyptians, Arabs, and Persians were acquainted with cane sugar over 1100 years ago. The cane is now cultivated in the West and East Indies, in the Southern States, and in South America.

In the old method of manipulation the cane, which contains up to 18 per cent. of its weight in sugar, was crushed between rollers, the expressed juice treated with milk of lime to neutralise acidity, filtered and evaporated to obtain the crystals. The solid was separated by drainage in perforated casks, and the mother liquor—which contains various substances

which prevent complete crystallisation—appeared on the market as treacle or molasses, or was fermented to make rum. With modern mechanical and chemical developments the industry has been brought to a state of great efficiency. The introduction of evaporating pans and similar plant has effected marked economy in fuel; the crystals are separated by centrifuges, resulting in great saving of time, and a leaf has been taken from the book of the beet sugar manufacturers by the employment of a diffusion process to replace the crushing. The cane is shredded and soaked in water, the sugar diffusing through the cell walls of the cane into the water, and the yield is enormously increased.

The process of refining crude sugar generally consists in dissolving it in hot water—blood being added to very crude sugars to carry down impurities in coagulating—filtering, decolourising by the action of animal charcoal, and evaporating to crystallisation. The products are separated into various grades according to purity. As an instance of the value of scientific control in sugar-refining processes, we may mention that one concern has for many years past effected a saving of between £75,000 and £100,000 a year as a return for an expenditure of £20,000 a year on its laboratories and staffs of chemists.

Sugar was discovered in beetroot by Marggraf, a German chemist, in 1747, but it was not until 1801 that a factory was established for its extraction, the first being erected in Silesia by Achard. In the light of present-day events it is interesting to observe that the German industry received considerable impetus in its early years through the land blockade of Prussia, enforced by Buonaparte, which made the home production of sugar a necessity. Buonaparte also gave encouragement to the establishment of the industry in France, and it is now carried on in Russia, Holland, and other European countries. The juice of the common beet contains only a low percentage of sugar, but by careful scientific cultivation the yield has been steadily increased, so that some varieties give over 15 lb.

of sugar per 100 lb. of beet, instead of about 6 lb. or less. The yield of beetroot from the land has been increased by about 15 per cent., and the coal consumption in the process of extraction has been reduced by about 80 per cent. The exhausted substance is utilised for making feeding stuffs for cattle. In the early method of extraction the roots were cleaned and shredded, the shreds placed in woollen bags, and the juice squeezed out by hydraulic pressure. This practice still prevails in some places, but has been replaced in others by the cleaner and more efficient diffusion process. The roots are cut into thin strips which are exposed to the action of water; the sugar diffuses out into the water, leaving colloidal substances in the cells, the walls of which are impervious to colloids. The treatment of the juice is similar to that employed in the case of cane sugar, the yield of crystallised sugar being about 70 per cent. of the sugar in the root, the other 30 per cent. remaining in solution as molasses or treacle, to be sold as such or used to make rum.

Increased yields of sugar in the crystallised state, from both cane and beet, are largely attributable to the Osmose process, based on Graham's work on dialysis, and the Elution processes elaborated by Steffen and by Scheiblor. In the first process the sugar is allowed to diffuse through a parchment membrane into pure water, the substances which prevent crystallisation being unable to pass through the membrane. The solution obtained is then worked up for sugar and for potassium nitrate which accompanies it, while the remaining liquor goes to the distillery for the manufacture of by-products.

The Elution processes depend on the formation of the sparingly soluble calcium or strontium salts formed by sugar—calcium and strontium saccharates. These salts, obtained by various methods in pure condition from the sugar in molasses, are suspended in water and decomposed into sugar and calcium or strontium carbonate, as the case may be, by the action of carbonic acid gas.

Other such processes have been devised, but that

involving the use of strontium hydroxide is most largely employed.

#### COLD STORAGE.

A valuable by-product of the beet sugar industry is trimethylamine, which is obtained by distillation from the final residue or vinasses of the Osmose process, and also in large quantities from herring-brine by distillation with lime. It is a gas at ordinary temperatures condensing in the cold to a liquid which boils at 3.5 deg. Cent., and is used, as we have noticed before, in the place of ammonia, in the manufacture of potassium bicarbonate by a method analogous to the ammonia soda process. By heating its hydrochloride with hydrochloric acid, methyl chloride, an easily condensable gas, is obtained, and used for making certain dyes, and also as a freezing agent in the technical production of ice.

The preservation of food by cold storage is of great importance, and depends for its usefulness upon the availability of a large and cheap supply of ice. In the preparation of ice, advantage is taken of the heat absorption of boiling liquids. A gas that can easily be liquefied by pressure can be used as a freezing agent, provided that its other properties are not objectionable. The gas is liquefied by mechanical pressure, and is then allowed to evaporate under low pressure, the only heat available for its vaporisation being that contained by the water it is desired to freeze. The freezing agent is, of course, not destroyed, but can be recondensed and used over again. Gases in common use as freezing agents are methyl chloride, which liquefies at ordinary temperature under two or three atmospheres pressure, and boils under ordinary pressure at 24 Centigrade degrees below zero, ammonia gas, which liquefies under about six or seven atmospheres and boils under ordinary pressure at 33.5 Centigrade degrees below zero, carbonic acid gas, and cymogene (referred to in Chapter V.).



## CHAPTER XV.

## BREWING.

THE production of malted liquors was one of the first industries to recognise the value of scientific investigation in the elucidation of technological problems; but the industry has not alone profited—the field of work has proved so rich in discovery that an important domain of chemical science, the chemistry of fermentation, with its applications to the leather, tobacco, food and other industries, as well as to physiological science, has been opened up, primarily through the study of the principles underlying the practice of brewing.

Alcoholic liquors were brewed from grain stuffs in Egypt as early as the 4th Dynasty (B.C. 3000 to 4000), the beverages taking the place of wine in countries where the climatic conditions were unfavourable to the cultivation of the vine. Although the Egyptians had vineyards in the Nile Valley, it is probable that this restriction of area gave rise to the brewing of grain liquors in other less favoured parts. The earliest fermented liquor known in Britain was mead, made from honey; the production of beer from barley, and of cider from apples followed in the order indicated. All three beverages were in use in the South of England at the time of the invasion by the Romans, who are said to have considerably improved the manufacture of beer, which subsequently became the national drink of the country. In the Middle Ages rents were sometimes paid in malt or beer, and it is not without interest to note that one of the municipal appointments in the time of Queen Elizabeth was that of the ale-taster, a post held by the father of William Shakespeare at Stratford-on-Avon. Ale-tasters were required to examine

beer and ale to see that they were good and wholesome, and sold at proper prices. Public analysts may now be considered to carry on these duties, the custom of appointing ale-tasters having been discontinued in most places since beer and ale became excisable commodities.

In normal times about 35 million barrels of 36 gallons are brewed per year in the United Kingdom, involving the consumption of 50 million bushels of malt, over 60 million pounds weight of hops, more than a million hundredweights of specially prepared rice and maize, and about three million hundredweights of sugar.

The question of water supply is of great importance to the brewer, the nature of the impurities in the water used in mashing greatly influencing the quality of the product. The excellence of the pale ales produced at Burton has been traced to the existence in solution of large quantities of calcium and magnesium sulphates in the Burton well water. Stout and porter are better brewed with the softer water of London or Dublin, which does not contain the sulphates above mentioned. Sometimes the water in a locality can be so modified, by the addition of the requisite substances, as to be suitable for the brewing of different classes of beer; but the industry has been largely established in districts where the natural supply needs no special treatment.

The production of beer from barley involves three main operations: the conversion of the grain into malt; the preparation of an infusion of the malt called wort; and the fermentation of the wort by means of yeast. Malt is obtained by keeping barley in a moist atmosphere until the induced germination has proceeded to the requisite extent determined by examination of the grain. The product is then heated to a temperature above 50 deg. Cent. to stop germination. The infusion known as wort is made by mashing the finely ground malt with water, and keeping it for some time at about 67 deg. Cent. The resulting liquor, after straining through spent wort, is sterilised by boiling, when hops are added to impart

a bitter flavour, and to yield to the liquor certain preservative substances. The liquor is then cleared by settling, drawn off, cooled by "coolers" and refrigerators, and fermented by yeast.

The chief change taking place in malting barley is the production of an active body called diastase, which has the power to convert starch into sugar. During malting albuminoid substances are broken down into simpler bodies, and the starch undergoes modifications, assuming a form more easily attacked by the diastase. During the mashing operation the starch is converted by the diastase into a sugar, which is fermentable by yeast, thereby yielding alcohol. As the finished malt contains much more diastase than is necessary to convert all the starch present into sugar, starch, in the form of flaked rice or flaked maize, is sometimes added to the malt before mashing, the final result being an increased production of alcohol. When desirable the quantity of sugar in the wort can be increased by the direct addition of invert sugar or of glucose. Invert sugar, which contains nearly equal quantities of two fermentable sugars—dextrose and laevulose—is produced in large quantities for the use of brewers by boiling cane sugar with dilute mineral acids, whilst glucose, containing two sugars—dextrose and maltose—is made by the hydrolytic action of dilute mineral acids on starch, an intermediate product being dextrin (British gum). If the action of the acid were further prolonged dextrose alone would be the main product. Brewers' glucose contains 60–70 per cent. of fermentable sugars.

By boiling, the wort is sterilised and concentrated, certain complex protein bodies are eliminated by precipitation, diastatic action is stopped, and the flavouring and preservative materials are extracted from the hops which are added at this stage. Hops contain a yellow granular powder called lupulin, which is the most valuable constituent from the brewers' point of view. The lupulin in new hops may amount to 15 per cent. or more, and contains resins and bitter principles, which give a flavouring and

exert a preservative action on the beer; and certain volatile essential oils which also improve the flavour.

By fermentation with yeast the sugars in the wort are transformed into alcohol and carbonic acid gas. The growth of yeast, when supplied with suitable foods, and its remarkable action on certain sugars, have held the attention of scientific men for years. Liebig, in 1839, advanced the theory that yeast, an unstable nitrogenous compound, possessed the property of communicating this instability to sugars, causing them to decompose, but the living nature of yeast was not then recognised. About thirty years later Liebig's views were overthrown by Pasteur after a long controversy, and Liebig was compelled to make certain modifications in his theory. As the result of a series of epoch-making experiments, Pasteur came to the conclusion that yeast was an organism capable, under certain conditions, of maintaining its life without the aid of atmospheric oxygen, that element being derived from sugars, the presence of which fulfilled the conditions. The maximum fermentative power of yeast was therefore attained in the absence of atmospheric oxygen. This theory held the field until 1892, when the researches of Adrian J. Brown showed it to be untenable. In 1897 Buchner demonstrated that the living yeast cell is not necessary for fermentation, but that the clear liquid extracted from the yeast by heavy pressure served the purpose. He proved conclusively that the cause of the fermentation is an enzyme, which he called zymase. Further light has been thrown on the problem by Arthur Harden, who separated the active liquid into two inactive constituents—the enzyme and the co-enzyme—which, when remixed, became once more active. Harden has also shown the importance of phosphates in accelerating the change. To summarise: the living yeast contains and reproduces an active non-living body which is capable of converting sugars into alcohol and carbonic acid gas. The yeast grows at the expense of certain foods present in the wort.

*Utilisation of Waste Products.*—Dried yeast is used as a cattle food, and as the source of an excellent substitute for meat extract. Carbonic acid gas is compressed and used for the aeration of beer and mineral waters.

## CHAPTER XVI.

## ALCOHOL, WINES AND SPIRITS.

ALCOHOL is one of the most important chemical products. We have already referred to it as a solvent, in which capacity it is of great service to the chemist in the laboratory as well as in industrial operations involved in the manufacture of transparent soap, varnishes, French polish, collodion, and celluloid. It is not only as a solvent, however, that it figures extensively in the arts and manufactures. It is used in the technical preparation of chloroform, iodoform, fulminates, ether, acetic acid, and many other bodies. For certain purposes—such as the production of some kinds of whiskey and brandy, and of liqueurs, and in the manufacture of scents, fine chemicals and drugs—only alcohol of a considerable degree of purity can be used, and the expense is correspondingly high.

Alcohol is made from the cheapest starchy materials available, such as potatoes, maize, turnips, molasses. The raw material is mashed with about 5 per cent. of malt, and fermented in the usual way. After distillation in a Coffey still, the spirit is diluted with water, filtered through wood charcoal to remove fusel oil and redistilled through a fractionating column. The products are separated into three grades: first runnings, and first and second quality spirits. The first runnings, containing about 95 per cent. of alcohol with a small quantity of aldehyde, may be used for burning and in manufactures where the impurities give rise to no deleterious effects. The first and second qualities, which are 96 to 97 per cent. in strength and contain only traces of aldehyde—the second quality also containing a small quantity of fusel oil—are known as silent spirit, because they afford no evidence of their source. These qualities

are used for drinking purposes—liquours and factitious brandy and whiskey—and for pharmaceutical preparations.

Absolute alcohol, containing 99 per cent. or more of alcohol, is obtained by dehydrating the finer spirits by redistilling with about half their weight of quicklime, whilst 100 per cent. alcohol may be prepared by the addition of a small quantity of metallic sodium to absolute alcohol and further redistillation.

The denaturing of industrial spirit—rectified spirit and first runnings—consists in adding to the alcohol, to render it undrinkable, some substance or substances which cannot be profitably separated, and which have the minimum harmful effect in the processes demanding the use of such spirit. Were it not for the fact that in most countries the Governments permit the sale and use of denatured or undrinkable spirit free of duty, the high duty on such spirit would render its use in ordinary manufactures prohibitive from the point of view of economy, and the absence of such facilities would prove a great hindrance to the industries concerned.

Methylated spirit is duty free, and may be used instead of rectified spirit—spirits of wine—in the manufacture of chloroform and varnishes, for preserving anatomical specimens and for many other purposes. It was originally made by adding about 10 per cent. of methyl alcohol—wood spirit—a product of the destructive distillation of wood, which has a sharp fiery flavour and contains substances disagreeable both to taste and smell. The presence of wood spirit, however, has little or no effect on the industrial uses of alcohol, from which, moreover, it cannot be profitably removed. The main use of wood spirit, therefore, is for denaturing purposes; but it is also employed as a solvent for resins and in the manufacture of dyes, its characteristic component  $\text{CH}_3$ , appearing in this rôle as a constituent of the intermediate products methylaniline and dimethylaniline, bases largely used for the production of basic dyes, such as methyl violet—the colouring matter of recording, copying, and typewriting inks—malachite

green, and methylene blue. The processes for the extraction and purification of wood spirit, however, were in the course of time so far improved, that its purity eventually unfitted it for use alone as a denaturant; it is still universally used for the purpose, but with the enforced addition of other more disagreeable substances, such as—in the case of ordinary methylated spirit—not less than  $\frac{3}{4}$  per cent. of paraffin of specific gravity 0.800. For some manufacturing purposes the paraffin is a disturbing factor, causing turbidity on mixing with water, and being unsatisfactory in other respects. To obviate these disadvantages, various denatured spirits are now made, containing from 2 to 10 per cent. of wood spirit with a smaller quantity of other substances of unpleasant taste, the choice being determined according to the purpose for which the spirit is to be employed. Thus, in the manufacture of transparent soap, a spirit denatured with wood spirit, castor oil and caustic soda is useful; in making mercury fulminate, a mixture of wood spirit with pyridine bases forms a suitable denaturant; and in making celluloid the spirit may be mixed with wood spirit, camphor, and benzene. Other denaturants include toluol, xylol, wood vinegar, turpentine, animal oil, chloroform, iodoform, and ethyl bromide, according to the needs of the industry for which the spirit is required.

*Wines.*—The production of wines by the fermentation of grapes is an industry of great antiquity. Several words in Hebrew are translated in our Old Testament as wine, and we find it associated with Noah, who, when he began to be an husbandman, planted a vineyard, drank of the wine and was drunken. Fermented grape juice was a beverage of the ancient Egyptians five or six thousand years before our time.

Wine is made by allowing the juice of grapes to ferment spontaneously, the organism inducing the change occurring plentifully in the air dust of vine-growing countries, and speedily infecting any sugary liquor freely exposed to the air. When white wine is the product desired, all the seeds and husks



of the grapes are carefully excluded, because it is from these that the colouring matter of red wines is extracted by the alcoholic liquid produced by fermentation. The seeds and husks also give up a small quantity of tannin, which acts favourably as a preservative of the red wines, and prevents ropiness. Sparkling wines, such as champagne, are made by dissolving sugar in a still wine and allowing it to undergo secondary fermentation in the bottle. Ordinarily, wine consists of a mixture of alcohol and water, containing from 7 to 17 per cent. of the former, together with smaller quantities of sugar, bitartrate of potash, glycerine, and other bodies, including traces of flavouring matters. If a sugar solution contains much more than 30 per cent. of its weight of sugar it cannot be fermented by yeast. A solution of alcohol of 16-17 per cent. strength also inhibits the action of yeast, and it follows, therefore, that fermented liquor cannot contain more than this percentage. Should a wine of greater strength be desired, it can be obtained only by the addition of stronger distilled spirit. Thus the strongest port wine, as produced by the ordinary fermentation, contains not more than 16 to 17 per cent. of alcohol, but it can be "fortified" if necessary by the addition of absolute alcohol or rectified spirit in the proper proportion. For this purpose it is desirable to use the strongest alcohol obtainable, as if a weaker, *e.g.*, less than 90 per cent., were used, the water necessarily added with it would dilute the other ingredients of the wine to an abnormal extent, and modify unfavourably its original characteristics.

*Spirits* may be divided roughly into two classes, (1) pot-still spirits, including brandy and whiskey; and (2) gin spirits, made by the suitable treatment of plain rectified spirit or alcohol. The manufacture of spirits was made possible only by the discovery of the process of distillation, and is not, therefore, of such antiquity as the wine and beer industries. The products differ from fermented liquors from which they are produced, mainly in the larger content of

alcohol, in the absence of non-volatile matter, and in the possession of certain distinct flavouring matters, either occurring naturally or added purposely. Cognac brandy is made by distilling from a pot the fermented juice of a small variety of grape, the alcohol passing over among the first products of the distillation. The spirit contains about 50 per cent. of alcohol, and owes its aroma and flavour to small quantities of capric (cænanthic) ester derived from the wine. The colour of genuine old brandy is due to colouring matter extracted from the wood of the casks in which it is stored, its astringent flavour being due to tannin from the same source. New brandy is coloured to resemble the old by the addition of caramel (sugar—generally starch sugar—heated to about 190 deg. Cent.), astringency being sometimes imparted by an infusion of tea.

Whiskey is made from malted barley, or from a mixture of unmalted and malted grain, the mixture being dried over a peat fire, from which the whiskey derives its smoky flavour. By a washing operation similar to that practised by brewers, a wort is produced which is cooled quickly by refrigerators and fermented by purified brewers' yeast, as completely as possible, at a low temperature. These conditions combine to ensure the production of a good liquor free from sourness, and with the minimum of wasteful and objectionable impurities such as fusel oil and aldehyde. When the fermentation stops, the liquor is distilled from a large copper still—up to 12,000 gallons—sometimes with the addition of soap to prevent undue frothing until all the alcohol has passed over. The distillate from this operation known as "low wines" is poor in alcohol and requires a second distillation. The residue remaining in the still contains a small quantity of lactic acid, which is often recovered and used as a substitute for acetic and tartaric acids in processes where a weak acid is required, and where the chemical nature of the acid is not of first importance. The second distillate is collected in three fractions called "fore-shoots," "clean spirits," and "feints." The clean

spirit is a strong whiskey containing about 60 per cent. of alcohol. It is generally diluted with water to about 40 per cent. before being sold to the customer, the minimum being fixed by Act of Parliament (1879) at 37 per cent. by weight. The fore-shoots are highly impure, containing fatty acids and other substances, while the "feints" consist chiefly of fusel oil, a mixture of higher boiling alcohols, used in recent years as a raw material in the production of synthetic rubber, and also as a solvent. The "spent lees" remaining in the still is a waste for which as yet no useful application has been found.

British brandy and whiskey prepared in a similar way from potato starch need to be freed from a rather larger percentage of fusel oil than does barley spirit.

Rum, which is made by fermenting treacle or molasses, and twice distilling the product, owes its flavour to formic and butyric esters, and is coloured either by ageing in wood, or artificially by means of caramel.

The plain spirit, *i.e.*, a mixture containing water and alcohol only, which is used to make gin and liqueurs, is produced by fermenting a mixture of malted and unmalted grain, and distilling the resulting alcoholic liquor or "wash" through a special fractionating apparatus such as the Coffey still. When distillation takes place from a pot-still little fractionation occurs, and a large proportion of the lower and higher boiling substances pass over with the alcohol, necessitating a second distillation; but by the use of a contrivance such as the Coffey still, which is too complicated for description here, the greater proportion of the impurities can be eliminated by one distillation.

Gin is made by adding some substance, such as juniper or liquorice root, to the spirit, and re-distilling from a pot, when the distillate passing over carries with it the flavouring matter extracted from the root. Liqueurs are made by dissolving large quantities of sugar in the alcohol with various flavouring and colouring materials.

## CHAPTER XVII.

## TOBACCO, INKS, PENCILS, &amp;c.

TOBACCO is cultivated in many countries, especially in Virginia and the Southern States, in Mexico, Cuba, and the West Indies, in Asia Minor and Persia, in India, China, and Borneo, and in South Africa, and affords scope for the botanist, biologist, and chemist, both in the plantations and in the factories. In the days of Columbus the natives of the West Indies smoked the rolled leaf, the Mexicans and North American Indians used pipes, and the Aztecs and Hispaniolan Indians applied forked tubes to the nostrils. Tobacco was introduced into Europe by Hernandez de Toledo in 1559, into England by Sir John Hawkins in 1565, and its use speedily became very general in spite of all forms of opposition. Smoking was the butt of the wits, denounced by the clergy, and condemned by rulers and popes, offenders being subject to severe punishment. In Turkey it was a capital offence, and in the canton of Berne was prohibited as an addition to the decalogue. In England King James I. issued a "Counter-blaste to Tobacco," in which smoking was described as "a custom loathsome to the eye, hateful to the nose, harmful to the brains, dangerous to the lungs" . . . as "resembling the horrible smoke of the pit that is bottomless;" but although often the subject of violent diatribes, it remains at the present day a most popular luxury among both rich and poor, and we may contrast the views of the Stuart King with those of Kingsley indicated in "Westward Ho!" "When all things were made none was made better than Tobacco; to be a lone man's Companion, a bachelor's Friend, a hungry man's Food, a sad man's

Cordial, a wakeful man's Sleep, a chilly man's Fire. There's no herb like it under the canopy of Heaven."

Tobacco is rarely prescribed in medicine or employed in pharmacy; but it is well known that smoking in moderation acts as a sedative, and is often beneficial in promoting expectoration in cases of asthma. Snuff, which is prepared from the ribs and stems of the tobacco leaf, is occasionally recommended to excite the secretion of mucus from the nasal membrane. The absorption of very small quantities of nicotine is stimulating to mind and body, but in excess the effect is depressing, narcotic, and injurious to the sight. Much depends upon the constitution of the smoker, habituation, and other circumstances. But we have digressed from our object. The industry is an important one from the financial standpoint. In normal times we spend between four and five million pounds on imported tobacco—more than twice the expenditure on dyes—and the smoker pays very heavily to the Exchequer for his luxury. He is protected, however, by the inspection of imported tobacco by the Government laboratory. Many thousand samples are examined annually, in accordance with the legislation forbidding adulteration or excess of moisture, offenders being liable to heavy penalties. Tobacco was formerly much adulterated with leaves of rhubarb, cabbage, dock and the like, as well as with sugar, starch, and gum; but although sweetening matters such as sugar, treacle, liquorice, and glycerine are occasionally present in imported tobacco, adulterants are now comparatively rarely detected.

The chemical composition of tobacco is highly complex, the determinable constituents numbering over twenty. The quality of the leaf is attributed to the nature of the soil where it is grown, though the finished product must remain largely a matter of taste. The methods of manufacture depend on the variety of tobacco and the purpose for which it is intended; and the processes are supervised more and more by men of science who can render useful assistance in many ways, such as the prevention of mouldiness

and the utilisation of waste. The leaves, when harvested, are allowed to wither to a certain extent, and then undergo shed-drying or sweating in moderate heaps covered with matting. The leaf cells transpire carbohydrates, albuminoid matters become converted into amides, and the heat generated effects the drying of the leaves, which then undergo fermentation in bundles arranged in large heaps. Tons of tobacco are thus allowed to decompose rapidly at a temperature usually kept below 50 deg. Cent., the bundles being turned about so that all are equally affected. Suchsland is stated to have prepared cultures of the bacteria of the fermentation, and to have transferred them from fine West Indian to German tobacco in the course of fermentation, with remarkable improvement to the latter.

The leaf as imported to this country is subjected to secondary fermentation after the addition of 5 to 25 per cent. of water, and is dried or stoved on heated open trays, or in closed ovens subjected sometimes to injections of steam, different methods of treatment affecting the flavour of the product. The content of nicotine in the leaf varies from 1 to 5, though it is sometimes as high as 8 per cent.; a single cigar often contains a deadly dose, but it retreats from the heat as the tobacco burns and accumulates in the stump or butt. By passing a current of steam through a mixture of lime and tobacco dust, neutralising the resulting liquid with sulphuric acid, and adding caustic potash, nicotine is liberated and may be dissolved in ether, the solution yielding almost pure alkaloid, which is employed in the manufacture of insecticides for horticultural purposes.

We propose now to deal with a few industries under scientific control which employ chemical products, and relate to commodities in everyday use.

*Inks.*—In early times the thoughts and actions of men were incised on stone, impressed on clay or wax, or carved on ivory, metal or wood; but with the introduction of papyrus, which we have mentioned in

the chapter on cellulose, characters were formed by the application of coloured fluids by means of a brush or reed. The word "ink" is associated more closely with the more ancient methods, being derived from the Greek *encaustos* (burnt in), and from the Latin *encarustum* (the purple-red ink used by the later Roman Emperors). The oldest writing material appears to have been composed of very finely divided carbon in a solution of an adhesive substance, which held the carbon in suspension and fixed it to the papyrus. Ink of this sort has been found on ancient Egyptian papyri, and was no doubt also in use in China at least as early. Carbon inks are permanent and very resistant to chemical action, but there is a tendency for the pigment to sink in the liquid unless it is frequently stirred. Printing inks also consist mainly of carbon with well-boiled drying oils and soap or resinous matter. For ordinary writing purposes, however, carbon inks were superseded centuries ago by iron-tannin inks, prepared from a decoction of galls with copperas and gum arabic, formerly home made, but now produced in common with many other domestic requirements on an industrial scale. The action of the tannin—from the decoction of galls—on the copperas produced a precipitate, which, being insoluble, formed a deposit, but manufacturers avoided these conditions by excluding air to prevent oxidation, and by adding soluble colouring matter. Good writing ink should remain sweet and fluid when exposed to air, should be permanent to light under ordinary atmospheric conditions, and not contain an excess of free acid which would injure the pen and paper, though the ink is not always to be blamed for these contingencies. In the middle of the eighteenth century logwood was added; in many cases it replaced the tannin entirely, and still forms the basis of some inks. Coloured inks have also been prepared with cochineal and indigo, and with the introduction of coal tar dyes a large variety of easily running inks, specially suitable for stylographic and fountain pens, have been rendered available, though it should be remarked that they are not regarded as so permanent

as the iron-gallo-tannates. Many typewriter ribbons are prepared with coal tar dyes, and are therefore open to this objection, the ink being fairly easily removed by chemical means. Inks highly sensitive to tampering are employed for bankers' cheques, and the detection of forgeries often depends on the effects produced by treatment with various chemical reagents. Copying inks are concentrated writing solutions, usually containing two or three times the amount of colouring and thickening matter. It is probably no news to engineers that James Watt invented the copying press, the patent for which was granted to him in 1780. He employed an ink prepared from a decoction of Aleppo galls, green copperas and gum arabic, which is much the same as the inks now used for the same purpose, except that they contain soluble dyes, dextrin or sugar, and in some cases glycerine. Iron tannin inks, when exposed to the air, become oxidised and insoluble, so that they cannot be copied.

The juices of various plants have long been utilised as marking inks, such plants including the ink plant of New Granada and New Zealand, the cashew nut, the Indian marking nut and others. Modern marking inks, which should withstand the action of soap and alkaline and acid liquids, mainly consist of solutions of silver nitrate coloured with lampblack and thickened with gum. Salts of gold, platinum, manganese, and of other metals have been used for the same purpose.

*Pencils.*—We have already noted the use of the brush for applying characters to papyrus. The word "pencil" is derived from the Latin *penicillus*, a small tail. The use of charcoal and similar materials followed and, at an early date, metallic lead was employed to mark parchment and papers; hence, the term "blacklead" as applied to pencils, denoted the blacker mark of graphite or plumbago. As a matter of fact, the graphite used for making pencils consists almost entirely of carbon and contains no lead. It has been employed for this purpose since the seventeenth century, and for a long time was obtained almost exclusively from the Borrowdale mines in



Cumberland, being mined in compact grey-black masses, cut into thin plates, then into rectangular sticks and cased in wood. The mine was guarded by an armed force, and, to maintain the monopoly, an Act was passed restricting the working to only six weeks in the year; for the remainder it was flooded to prevent theft. The best quality was exhausted early in the nineteenth century, and the pencil manufacturers turned their attention to utilising accumulations of waste from cuttings of the original masses, which were crushed and mixed with other materials.

One of the results of such experiments was the introduction of varying degrees of hardness in which respect the native graphite was never uniform. Conté, of Paris, is credited with the method now generally employed, of making pencils from finely ground graphite mixed with varying proportions of clay, allowing for fourteen degrees of hardness and softness ranging from 6 H to 6 B with HB (hard and black), and F (firm) as the middle degrees.

Graphite has since been found in many parts of the world. The crystalline variety occurs in Ceylon, but is not sufficiently black for pencil-making; the massive, which occurs in Bohemia, Bavaria, and Mexico, is much blacker. It is ground very fine, mixed with water, and passed through tanks to allow the heavier particles to fall, the finer particles passing on to five or six successive tanks, when the necessary degree of fineness having been obtained, it is mixed with suitable clay which has been washed in the same manner. The mixture is submitted to further grinding, squeezed in bags to remove superfluous water and forced through tubes to produce strips of the required shapes and sizes, which, when dried and baked, are ready for casing in wood.

The wood mostly used for making pencils is that of red cedar, not the cedar of Lebanon, but the *Juniperus Virginiana* which grows in Florida, Alabama, and Tennessee, and lends itself well to the purpose on account of its soft character and straightness of grain. It is usually cut into short thin

slats of the length of a pencil, though sometimes of several lengths, and sufficiently wide for making from two to six pencils. The slats are grooved to receive the lead and, when glued together, can be cut into the corresponding number of pencils, which are then smoothed by machinery, polished, stamped with the letters indicating the degree of hardness, and the makers' name, tied into bundles, and generally prepared for sale. Coloured pencils are made from special clay finely ground with colour, such as Prussian blue, or vermilion, and mixed with a binding material, pressed into sticks which are toughened by boiling in a mixture of special fats and waxes before they are placed in the slats. For copying-ink and indelible pencils, an anilino dye is used, the colour being soluble in water in order that impressions may be taken on tissue paper. With the demand for pencils steadily increasing and the supply of suitable cedar becoming quickly exhausted, manufacturers will be obliged to use other woods, or users must be content with mechanical pencils. The industry is restricted to comparatively few firms, the majority being of long standing. Details of manufacture are largely kept secret, but enough has been said to indicate that the industry owes much to chemical science, in the selection, mixing, and general treatment of materials, and to mechanical science in the invention of labour-saving machinery for the processes involved.

Other domestic requirements, such as blacklead (stove polish), and blacking, for leather, are now produced under scientific control. *Black lead* for producing a polished black surface on iron is made from the massive graphite. *Blacking* is made of a variety of materials and consists essentially of some black pigment, such as animal charcoal (bone black), incorporated with substances capable of taking a polish by friction. A mixture of bone black, sperm oil, molasses and vinegar forms a typical blacking, while other kinds contain starch as ground material with tannate of iron as colouring agent, and gum arabic as a binding material.

## CHAPTER XVIII.

## GASES.

IN the article on coal, we gave a brief description of the manufacture and purification of one of its principal decomposition products—coal gas. Before drawing our work to a conclusion, we propose to say something of other gases, little known to those who do not use them, and far simpler in their constitution than coal gas. Discovered by science, their manufacture is the outcome of scientific investigation, and not the mere retorting of a complex naturally occurring substance.

The word gas is said to have been introduced by the Flemish chemist, Van Helmont—sixteenth century—being associated with the Dutch *geest*, a spirit or ghost, Danish and German, *geist*, from the same root as the Anglo-Saxon *gaeslic*, ghastly. To the mediæval mind, the air was a mystery, something supernatural: it could not be seen or smelled, but could be felt and heard. Gradually the idea of the material nature of the air was developed by the schools, but owing to the vague nature of the entity concerned and the difficulty of handling it, little progress was made with experimental investigation until the middle of the seventeenth century. No variety was recognised and everything of the nature of air was classed as air, until the advent of methodical experiment and logical deduction laid the foundations of this fundamental department of knowledge.

A gas is physically the simplest form of matter; the laws governing its behaviour are less complex than those regulating the conduct of solids and liquids. To the recognition of this fact and the application of the principle of defeating the weakest enemy first, science

owes many of its most wonderful advances, such, for instance, as we find in the application of the laws of gases to substances in dilute solution. The extreme fluid elasticity of gases and vapours and their high co-efficient of thermal expansion render them invaluable to the engineer. The nature of explosion, the problems encountered in aeronautics, in meteorology, in the study of acoustics, are all closely connected with the properties, both statical and dynamical, of substances in the gaseous state.

Until the middle of the seventeenth century, the philosophers—students of nature—affected to despise experiment, their opinions being based on observation. The alchemists—seekers after the universal solvent, the philosopher's stone and the elixir of life—lovers as they were of theory and mysticism, extolled the experimental method by which they hoped to secure wealth and the extension of life. Modern experimental science may be considered as the outcome of one of the controversies between two factions of the former, combined with the overthrow of the methods of the latter. A discussion arose between the plenists, or Cartesians, who denied the possibility of a vacuum, and the Vacuists, who maintained that there was no reason why a vacuum should not exist. Robert Boyle, born in 1626, "son of the Earl of Cork, and the father of modern chemistry," flourished at the time of the plenist controversy, and the problem attracted him to physical science, especially the study of the properties of air. In 1658 he constructed the pneumatical machine—air pump—which was destined to be of primary importance in many of his subsequent experiments. His original aim being to obtain a vacuum, he made with its aid some significant discoveries. He demonstrated air pressure, and elucidated the volume pressure relations of gases. His law—viz., that, at a constant temperature, the volume of a given quantity of gas varies inversely as the pressure—was rediscovered independently a few years later by Marriotte, a Frenchman. Boyle's speculations on the chemical nature of air, founded on many observations, including the gain in weight of

metals on calcination, contributed to the advance of knowledge in his time, but the difficulty of pioneer work on an invisible and almost intangible medium limited such observations to the phenomena of combustion and respiration. In 1661 appeared, anonymously, "The Sceptical Chemist," a book which criticised the teaching of the alchemists and deprecated their method of expression and the ambiguity of their doctrines. As the author of this production Boyle did much to sweep away the cobwebs of mysticism. He was an early member of the "Invisible College," a body much attacked in its infancy for encouraging the investigation of Nature—then regarded by many as rank horesy—which eventually became our premier learned society, the Royal Society of London. His researches were mainly on "air," and there is little doubt that he prepared the gases now known as hydrogen, carbon dioxide, and hydrogen chloride; but he did not observe their characteristic properties. His work, however, marked the beginning of a new era in natural philosophy, his doctrine showing that scientific advances were made not by theory or practice alone, but by the application of both.

The discoveries and teachings of a genius have not infrequently been overshadowed by those of a greater and better-known contemporary. This was the case with John Mayow, a medical practitioner of Bath, who, in his experiments on air and his deductions therefrom, was ahead of the workers of his time. He recognised the existence of different kinds of gases in the air, and prepared a gas—nitric oxide—by the action of nitric acid on iron. He observed its action on air, but failed to see the analytical possibilities of the discovery. Boyle and Newton held the field in natural philosophy, and Mayow received little attention. Stephen Hales (1677–1761) prepared a large number of gases, but regarded them all as modifications of air, and failed to make use of the facts he accumulated. When, however, Joseph Black (1728–1799) discovered carbon dioxide, and Daniel Rutherford (1749–1819) isolated nitrogen, both

realised that those gases were distinct in their nature from air.

Then followed the epoch-making discovery of oxygen by Joseph Priestley and Carl Wilhelm Scheele, a Swedish chemist, working independently. Priestley also invented the eudiometer. Henry Cavendish (1731-1810) made the first analysis of air, devised the electric spark method of combining nitrogen and oxygen, thus laying the foundation of a very modern industry, and determined the composition of nitric acid. Cavendish proved the compound nature of water; determined its quantitative composition, and also examined thoroughly the fixed air—carbon dioxide—of Black.

All these eighteenth century investigators expressed their views on the action of air and combustion in terms of the phlogistic theory of Becher and Stahl, and it remained for Antoine-Laurent Lavoisier, the French savant, who fell a victim to the guillotine in 1794, to free them from this incubus and to develop the new theory wherein oxygen was assigned its proper rôle as a constituent of air and a supporter of combustion.

Thus the composition of air—as a mixture of oxygen and nitrogen with small quantities of carbon dioxide and water vapour—and the explanation of the nature of combustion were gradually established. To these early workers, and especially to Priestley, Cavendish, and Lavoisier, chemical science and industry owe an irredeemable debt. Out of chaos they produced order, and paved the way for the work of Avogadro, Clark Maxwell, and Clausius. No new essential constituents of air were discovered until the last decade of the nineteenth century, when Rayleigh and Ramsay, as an outcome of the measurements, by the former, of the density of nitrogen from various sources, including atmospheric, discovered five new chemically inert gases—Argon (without energy), Neon (new), Helium (Sun), Krypton (hidden), and Xenon (stranger)—no compounds containing these elements being as yet known.

*Hydrogen* —The discovery of hydrogen is usually

attributed to Paracelsus, a Swiss physician and chemist—fifteenth to sixteenth century. Its explosive properties were known to Lemery about 1700, but it was not until seventy or eighty years later that Cavendish demonstrated the individuality of the gas, and showed its relation to water. It is prepared in the laboratory by the action of a metal such as zinc or iron on dilute sulphuric acid, this being, in fact, the method by which it was first discovered, and it is obtained in a much purer state, when necessary, by the electrolysis of barium hydroxide. Traces of oxygen are removed by passage over hot copper shavings or platinised asbestos, the issuing gas being dried by means of calcium chloride, or of phosphorus pentoxide.

The properties of hydrogen bear no resemblance to those of any other element. It is colourless, odourless, tasteless, specifically lighter than any other known substance, very sparingly soluble in water, and capable of forming explosive mixtures with air or oxygen, with chlorine and fluorine. It has also the property, in the presence of finely-divided metallic nickel, of combining with certain bodies that are chemically unsaturated. Its density is less than one-fourteenth that of air, and its lightness and buoyancy render it of great value for use in airships and balloons. Provided that it is sufficiently pure, the two main advantages over coal gas for this purpose are superior lifting power and the absence of deleterious effect on the material of the envelope.

As a constituent of ammonia, hydrogen has in recent years been largely used in Germany in a process for the fixation of nitrogen, whereby the combination of the two gases, under high pressure—up to 200 atmospheres—at a temperature of 500 deg. Cent., is effected by the action of certain catalytic agents, such as osmium, uranium, iron, manganese, or tungsten. The efficiency of the catalysts is enhanced by certain compounds of the alkali or alkaline earth metals; but catalyst "poisons" also exist, and these are many and various. The gases must be freed from these substances, the most obnoxious of which

are compounds of sulphur and the hydrides of arsenic and phosphorus. The ammonia is separated by liquefaction, produced by strong cooling, or, in certain cases, by solution in water. This process was devised by Habor, is worked by the Badische Anilin und Soda Fabrik, and promises to become one of the chief methods of producing nitrogen. It need not stop at this stage, however, for through the work of Ostwald a mixture of air and ammonia gas, under proper conditions, with platinum, as catalyst, yields nitric acid, and the process may be developed by proper regulation to yield ammonium nitrate, a substance of high value as a fertiliser.

The third important use of hydrogen is, as we have observed in a previous article, in the hardening of fats, by direct action in the presence of finely-divided metallic nickel. According to the method of Sabatier and Senderens certain fine chemicals are now made by the nickel method of hydrogenation, and this also is likely to find extended application in industry.

With these developments it has become necessary to find means of producing hydrogen in large quantities at low cost. Owing to the expense of raw materials, and the difficulty of securing a convenient cycle of operations whereby the starting materials may be recovered, production by the action of metals on acids is not to much extent carried out on the works scale, though the method may occasionally be used for military purposes. Many patents have been taken out for the manufacture, and we will refer to some of the more important of them:— (1) By the action of steam on red hot iron, iron oxide is formed, and hydrogen is set free. It is then purified from dust, sulphur compounds, carbon dioxide, &c., by suitable scrubbing treatment. The iron oxide is reduced when necessary by replacing the current of steam by one of water-gas, the residue from this reaction being a source of nitrogen—Messerschmitt process. (2) By freeing water-gas from carbon dioxide, by means of lime or caustic soda, and subjecting the residue to the extreme cold produced by boiling liquid air, nitrogen and carbon



monoxide are liquefied, leaving the hydrogen in the gaseous state—Linde-Frank-Caro process. (3) By the electrolysis of the chloride or hydroxide of an alkali. (4) The decomposition of acetylene—prepared from calcium carbide and water—by heating electrically. Hydrogen is prepared for Zepplins by this method, which yields also a valuable by-product in the form of fine lampblack. (5) The gas is also produced by a number of other patent methods, mainly useful for military purposes. Hydrolith is calcium hydride, prepared by the action of hydrogen on calcium in the electric furnace, and on contact with water yields double the volume of hydrogen originally expended in preparing it. Hydrogenite is a mixture of five parts of ferrosilicon, four parts of slaked lime, and twelve parts of caustic soda. When heated locally a reaction takes place, and spreads throughout the mass with evolution of hydrogen. Both of these processes are due to Jaubert.

*Oxygen*, discovered by Priestley and Scheele, and named by Lavoisier, occupies about one-fifth of the volume of the atmosphere, and its properties as a supporter of life and combustion render it one of the most important of the elements. It is also the most abundant, representing about half the weight of the solid crust of the earth, and roughly eight-ninths of the water. It can be prepared in the laboratory by heating chlorate of potash either alone or with manganese dioxide, by the action of sulphuric acid on bichromates or permanganates, or by the electrolysis of dilute sulphuric acid, or of solutions of alkalies. On a commercial scale, Brin's process of heating barium monoxide—the analogue of lime—in dry, purified air to about 700 deg. Cent. under 10 lb. pressure, for long held the field. The oxide takes up oxygen, forming barium peroxide; the nitrogen is then pumped off, pressure being reduced to about 2 lb. Under these conditions the peroxide gives up its excess of oxygen, which in turn is pumped off and compressed into cylinders, reforming the monoxide, which is available again for the same cycle of changes. The method, however, has now been

largely replaced by the liquid air process, which depends for its utility on the ease with which air can be liquefied by the method of self-intensive cooling introduced on the Continent by Linde and into England by Hampson. Advantage is taken of the fact that a compressed gas cools on expansion. Air is compressed through a spiral, and allowed to escape from a jet. On issuing it is cooled, and in turn cools the air in the spiral by external contact. Thus the issuing gas becomes increasingly colder, until finally it issues from the jet in the liquid form. Liquid oxygen and liquid nitrogen boil at different temperatures, so that if the liquid air is fractionated the two gases can be obtained in a fair state of purity.

Oxygen finds application in medicine, in the chemical laboratory, and in the production of high temperatures, such as are obtained by feeding acetylene, hydrogen, and coal gas flames with the gas. Oxy-acetylene cutting and welding, oxy-hydrogen melting, including platinum working, the autogenous soldering of lead, and the use of lime-light, all depend on the production of an intensely hot oxygen-fed flame.

Ozone is a colourless gas, condensable in liquid air to a deep blue unstable liquid. Van Marum, in 1785, and Schönbein, in 1840, observed a peculiar smell in the neighbourhood of electrical machines in motion, and the latter found that it was due to a gas, which he named and found other means of producing. Andrews, in 1856, showed that the gas contained oxygen only, and Soret, in 1866, proved its composition, which is represented by the formula  $O_3$ . It is prepared by the action of a silent electric discharge on air or oxygen, a current of which is passed through a special apparatus called an ozoniser. The first of these was devised by Siemens in 1857, and since that date numerous patents, founded much on the same principle, have been recorded.

The commercial preparation resembles that on the small scale. The pure substance is not obtained in either case; not more than 25 per cent. of the oxygen is transformed into ozone under the best

conditions. The product is used in the sterilisation of water and to a less extent of certain foods.

*Acetylene* was discovered in 1836 by Edmund Davy, Professor at the Royal Dublin Society, during an attempt to isolate potassium by heating calcined tartar with carbon. He obtained a black mass, which in contact with water gave rise to an inflammable gas, and he suggested that if a cheap method could be found for preparing it, the gas might well be used as an illuminant. Its development as an industrial commodity was not realised until over fifty years later, but in the meantime several famous names came into the literature of the subject, including Hare, Berthelot, Wöhler, Kekulé, Vohl, and Sir James Dewar. Hare unknowingly made calcium carbide, and from it acetylene, by the action of water. Berthelot prepared metallic acetylides, and produced acetylene electrically from methane and also from carbon and hydrogen. Wöhler made calcium carbide by heating an alloy of zinc and calcium to a high temperature with carbon. Kekulé prepared acetylene by the electrolysis of the salts of dibasic unsaturated organic acids. Vohl obtained the gas by passing oils through red hot tubes, thereby laying the foundation of our modern oil-cracking processes. From American petroleum he obtained a gas containing 20 per cent. of acetylene. Dewar obtained acetylene by passing hydrogen through tubes made of retort carbon heated to whiteness by means of an electric current.

Acetylene is used, as we have already mentioned, in one of the processes for making hydrogen; as an illuminant in isolated dwellings, and in motor and bicycle lamps. It is invariably prepared by the action of water on calcium carbide, which comes on the market in the form of grey lumps, the product of heating lime with carbon in the electric furnace. The gas owes its position as an industrial product to the development of the electric furnace by Siemens, Bradbury, Cowles, and Moissan; but the credit for the realisation of the possibility of producing calcium carbide on a commercial scale belongs to

Willson, an American. In 1886, Cowles introduced a furnace lining consisting of a mixture of lime and carbon, and produced calcium carbide by the accidental overheating of this lining. No attempt was then made to utilise the discovery; but, in 1892, Willson, while working at Spray, with the object of reducing lime to obtain calcium for the reduction of alumina, prepared large quantities of the carbide, and, realising the potentialities of the substance, set up a works for its production.

*Nitrogen*, which forms about four-fifths of the air, is produced by the methods we have already indicated,\* especially the Linde-Hampson process, and is used in the synthetic preparation of ammonia, and of cyanamido and cyanides, from calcium and barium carbides respectively.

*Chlorine*, discovered by Scheele in 1774, and pronounced an element by Davy in 1810, is a heavy yellow poisonous gas of an extremely irritating odour. It is largely used in the sterilisation of water and in gold extraction, and has been employed as poison gas during the war. It is prepared by the action of manganese dioxide on hydrochloric acid, the oxide being recovered by the Weldon process. It may be converted into bleaching powder, through its absorption by lime, or liquefied by cold and pressure and stored in steel cylinders.

*Carbon Dioxide*, or carbonic acid gas, a waste product of the brewery, is used for aerating beer and mineral waters, and is sometimes employed as a freezing agent.

*Carbonyl Chloride*, or phosgene, prepared by the interaction of chlorine and carbon monoxide in the presence of animal charcoal, or of antimony pentachloride, or by the action of fuming sulphuric acid on carbon tetrachloride, is used in the manufacture of dyes, and has also been employed as a poison gas.

*Laughing Gas*, or nitrous oxide, is made by heating ammonium nitrate. It was discovered by Priestley in 1772, and is used as an anæsthetic in dentistry.

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\* Refer to Agriculture and Hydrogen.

We do not need to dilate on the relation between science and these products which are so obviously scientific in their conception, elucidation and development

## CHAPTER XIX.

## GOVERNMENT CHEMISTRY.

In the article dealing with Agriculture and Food, we have referred to the official agricultural analysts and public analysts, who are appointed under statutes to safeguard the quality of supplies of fertilisers and feeding stuffs, food and drugs; and we will now refer to other official chemists directly or indirectly concerned with industry.

In 1843 a laboratory was established at Somerset House, in connection with the Inland Revenue Department, to check adulteration of tobacco, and later a second laboratory was established at the Custom House for the examination of wines, spirits, and other imported articles liable to duty. In 1894 the control of these laboratories was entrusted to one Principal, and in 1897 the Excise Branch was transferred to a new building at Clement's Inn-passage. In 1911 the Government Laboratory was constituted an independent department under the Treasury, with a separate Parliamentary Vote, entitled "Government Chemist." The Laboratory undertakes investigations for every other Government Department, the greater part being carried out at Clement's Inn-passage, and in the branch laboratory at the Custom House. The Government Chemist also controls eighteen stations in different parts of the United Kingdom, where tests are made for revenue purposes. From a recent report, we gather that the work for the Department of Customs and Excise relates, mainly, to the assessment of duty and drawback, and to regulations and licences, in connection with the manufacture and sale of dutiable articles, such as beer, spirits, wine, tobacco, tea, sugar, coffee, cocoa, and preparations advertised for the cure or relief of human

ailments—commonly called “patent medicines.” The work for the Admiralty includes the examination of food substances, the analysis of metals and of contract stores; that for the Board of Agriculture and Fisheries refers largely to imported dairy produce and margarine, and includes—for the Fisheries Division—samples of river water believed to have been polluted and to have caused injury to fish, as well as the determination of the salinities of samples of sea water for the Permanent International Council for Exploration of the Sea. Samples of beer and whiskey are examined for the Central Control Board (Liquor Traffic); and of drugs, pharmaceuticals and contract supplies for the Crown Agents for the Colonies. Fire-clay and limestone from various districts are examined for the Geological Survey; lead glazes and enamels for the Home-office; drugs for the India-office, and stamps and inks for the Board of Inland Revenue. Investigations on preservatives in food are carried out for the Local Government Board; and on paper, pigments, gum, engineering and general stores for the Post-office; ink and typewriter ribbons for the Stationery-office; lighthouse stores for the Corporation of Trinity House; lime and lemon juice and ship’s stores for the Board of Trade; food supplies for the Army, drugs and surgical dressings, for the Army Medical Department, for the War-office; samples of varied character for the War Trade Department; samples of water for the Office of Woods and Forests; of contractors’ supplies and of water for the Offices of Works—London and Dublin; and samples referred by the magistrates under the Sale of Food and Drugs Acts, 1875 and 1899, and submitted by the Board of Agriculture, under the Fertilisers and Feeding Stuffs Act. The total number of samples examined during the year ended March 31st, 1916, was 383,892. The work has obviously an important bearing on industry and commerce, and entails the employment of a large technical staff, of which many members are required to be highly trained and competent chemists. As illustrating the value of their work, we may refer

to the examination of food for the armies in the field during the war, work essential in the interests both of the health of the troops and of the Exchequer. The food must be wholesome ; but the findings of the chemists will determine the cash value of the supplies : a deviation of, say, 1 or 2 per cent. of moisture in flour, biscuits or margarine, may involve a reduction of hundreds of pounds on a single contract.

Although the Government Laboratory constantly advises other departments, some possess their own laboratories for special purposes. The Admiralty has a staff under the Admiralty Chemist, and employs chemists in connection with the examination of various materials of construction and victualling stores. The Admiralty has also its duly appointed Adviser on Petroleum, as well as officers possessing special scientific experience, and professors of chemistry in the Royal Naval Colleges. The War-office, too, makes good use of chemists in many matters arising out of the conditions of modern warfare, and instruction in chemistry is given in the Royal Ordnance College, the Royal Army Medical College, the Royal Military Academy, and other establishments. Under the Ministry of Munitions, in addition to chemists engaged in an advisory capacity, there are considerable numbers in charge of the production of explosives in Government and controlled factories, and special staffs are appointed for research and inspection work.

Official analysts are appointed to the Home-office for toxicological work, as well as in connection with the Explosives Department and the Factory Department. The Local Government Board possesses a Department for the inspection of food and a staff of specially qualified inspectors to assist in the administration of the Alkali, &c., Works Regulation Act. The Metropolitan Water Board and the Rivers Boards in various parts of the country have their chemical and bacteriological laboratories, and so have the Sewage Boards and Works. The Scottish Office also appoints inspectors under the Alkali Act and Rivers Pollution Prevention Act.



The London County Council controls a considerable staff for chemical investigations, including gas testing, and the Board of Trade appoints the Gas Referees, in accordance with the Metropolis Gas Acts, to prescribe the apparatus and materials to be employed for testing the illuminating power, calorific power, purity and pressure of the gas, the mode of testing, and, in certain cases, the times of testing, the current prescriptions being published in the "Notification of Gas Referees." Other county and borough authorities make provision for the inspection of water and gas supplies. Chemists are also included in the staff of the Patent-office, and Assayers render responsible service in the Royal Mint and at the Assay Offices, as well as for the Bank of England.

The Scientific and Technical Department of the Imperial Institute conducts investigations for the Indian and Colonial Governments, chiefly relating to the composition and utilisation of raw materials. The National Physical Laboratory includes a Department of Metallurgy and Metallurgical Chemistry. Laboratories are attached to many public Institutions, such as the Davy-Faraday Research Laboratory of the Royal Institution, and those of the Lister Institute and the Royal Dublin Society.

The existence of this extent of official organisation in chemistry is little known to the general public, but it is obviously indispensable to the well-being of the community. The *personnel* of our chemical service includes many men of science of high repute in their professions who deserve well of their country, and it is essential that the conditions attaching to this service should be such that it will continue to attract chemists of the highest competence. We have endeavoured to make this list fairly comprehensive, but have not referred to India and the Overseas Dominions, where many chemists hold appointments analogous to those we have indicated; nor have we referred to the valuable work carried out by analysts in hospitals and public health laboratories, or the appointments held in the Universities and Technical

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Colleges, to which we look for the continued supply of lieutenants to meet our requirements in the various branches of chemical practice.

## CONCLUSION.

WHILE we have confined our attention mainly to the debts of industry to chemical science, we do not suggest that those due to physical and mechanical science should not be similarly acknowledged.

The art of engineering has been steadily built up through the ages, but modern developments are, in the main, directly attributable to the advance of science. In chemical industries, however, the processes of manufacture, in many cases, preceded the discovery of the scientific principles on which they were based. The ironmaster, the dyer, the soap and candle maker, the tanner, the potter, and the glass manufacturer, were in existence centuries before serious attention was paid to the science underlying their work. Conventions die hard, and for a long time there was little enthusiasm to take advantage of what science had to offer. It is freely admitted that the state of civilisation attained before the advent of modern science was far removed from the conditions of life of primitive man; but it is claimed that while science was so little developed, industry had to look to experience as the only basis to work upon. Experience, accumulated slowly and at great cost, had done great things; but the rate of progress in industry developed in the past century defies comparison with all the centuries combined since time was—so far as we know! Still, let us admit that the inheritance was great, and that even the alchemist preserved much that was good in chemistry, just as the monks of the Middle Ages preserved much that was good in classical literature and architecture. We have endeavoured to indicate the interdependence of science and industry on one another, and to show how frequently science—"the nursling of interest and the daughter of curiosity"—pursued for hor

own sake, has sooner or later proved her practical utility. Incidentally we have shown that though "Genius is of no country," British men of science, often in the face of small encouragement, have played their part in industrial development. There is no reason to depreciate the value of their work, or to pay much attention to the Jeremiahs who seem to delight in bemoaning the industrial and commercial position of this country but are seldom able to offer any constructive criticism.

Advancement may be the outcome of the labours of the consultant, the chemist on the works, the official chemist, or the professor; all have contributed their share to discovery and invention. In any case, it is certain that our industries have utilised their knowledge, skill and experience to a greater extent than has been generally recognised; otherwise much that has been done in the last three years would have been impossible, and our position would have been far worse than it is.

We feel that the apathy towards science prevailing before the war was more imaginary than real and, such as it was, is being overcome; that the general public is beginning to realise something of the importance of science in the affairs of everyday life, and that the time is at hand when the services of the man of science will be better understood and consequently more substantially rewarded. The men of science themselves are increasing in number and influence; their work lies more and more in the control of large scale operations, as well as in the laboratory. The time has passed when men feared to probe into the truth as if it were sacrilege, or to imagine things beyond certain knowledge and established fact, or to explore into realms of not only the improbable but the seemingly impossible, whence so much, with the aid of science, has been and is yet to be derived.

To-day, the arts and sciences go hand in hand: the engineer and the chemist, each recognising the limits of his own domain, though the line dividing them may often be difficult to define, co-operate with one

another and mutually assist in the solution of industrial problems. Now is the time for leaders of industry to see to it that the opportunity is taken of making good, wherever possible, the connecting link between science and practice. A thorough overhauling of methods and plant should keep our consulting chemists and engineers well employed in preparation for the future. There is no lack of good men, and soon there will be enough and to spare for permanent appointments on the works.

If in these articles we have been successful in indicating some of the triumphs of science in industry, and if our efforts have in any way conduced to a better realisation of the value of scientific thought and method, we may rest satisfied that our labour has not been in vain.

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